3. L. Ya. Malkes, N. P. Kovalenko, and Yu. M. Vinetskaya, Zh. Prikl. Spektrosk., 11, 854 (1969).
4. L. Ya. Malkes, R. A. Minakova, and T. P. Boronenko, in: Scintillators and Organic Luminophores [in Russian], VNII Monokristallov, Kharkov (1975), p. 44.
5. G. Drefahl and J. Plötner, Chem. Ber., 93, 990 (1960).
6. C. Wittig and U. Schöllkopf, Chem. Ber., 87, 1318 (1954).
7. A. J. Spezial and D. E. Bissing, J. Am. Chem. Soc., 85, 1888 (1963).
8. L. A. Kutulya, A. E. Shevchenko, and Yu. N. Surov, Khim. Geterotsikl. Soedin., No. 2, 250 (1975).
9. N. P. Shimanskaya, L. A. Kutulya, L. A. Kotok, T. F. Alekhina, A. E. Shevchenko, and T. P. Zubanova, Zh. Obshch. Khim., 47, 2046 (1977).
10. L. V. Subina and L. Ya. Malkes, Zh. Org. Khim., 1, 1040 (1965).
11. L. V. Shubina, L. Ya. Malkes, V. N. Dmitrieva, and V. D. Bezuglyi, Zh. Obshch. Khim., 37, 437 (1967).
12. L. A. Kutulya, A. E. Shevchenko, and L. A. Terekhina, in: Scintillators and Organic Luminophores [in Russian], VNII Monokristallov, Kharkov (1975), p. 54.
13. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen (1958).
14. S. V. Tsukerman, E. G. Buryakovskaya, Yu. S. Rozum, and V. F. Lavrushin, Zh. Prikl. Spektrosk., 8, 453 (1968).
15. L. V. Shubina, Author's Abstract of Master's Dissertation, Moscow (1966).
16. K. Friedrich and H. H. Henning, Chem. Ber., 92, 2756 (1959).

AZIRIDINYL KETONES AND THEIR HETEROANALOGS.

2.* SYNTHESIS AND STUDY OF 5,7-DIARYL-1,4-DIAZABICYCLO[4.1.0]HEPTA-4-ENES

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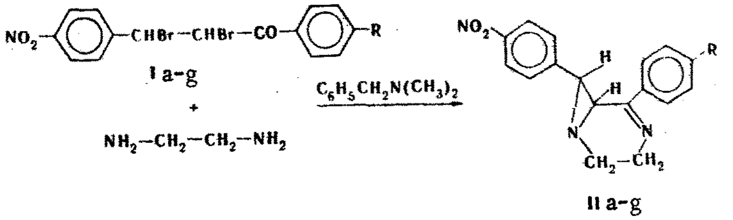
5-Aryl-7-(4-nitrophenyl)-1,4-diazabicyclo[4.1.0]hepta-4-enes (I), which have photochromic properties, were synthesized. The structures of the compounds were confirmed by data from the IR, PMR, and mass spectra. The acidolysis of I was investigated, and it was assumed that the mechanism of the reaction includes diprotonation of the bases, while the primary process is the formation of immonium salts. The structures of the photocolored forms of the salts and bases are discussed.

Continuing our study of cyclic anils of aziridinyl ketones [1], we synthesized a number of 5-aryl-7-(4-nitrophenyl)-1,4-diazabicyclo[4.1.0]hepta-4-enes (IIa-g), the interest in which is due to their clearly expressed photochromic properties.

The synthesis of II was accomplished by the method of Heine and Henzel [2] by the reaction of 1-aryl-3-(4-nitrophenyl)-2,3-dibromopropan-1-ones (Ia-g) with ethylenediamine in the presence of N,N-dimethylbenzylamine:



I-II a R=H; b R=CH_3; c R=CH_3O; d R=Cl; e R=Br; f R=NO_2; g R=C_6H_5

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*See [1] for communication 1.

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TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C *	IR spectrum, cm^{-1}						N found, %	Empirical formula	N calc., %	Yield, %
		$\nu_{C=N}$	ν_{asNO_2}	ν_{sNO_2}	ν_{Ar-NO_2}	$\delta_s N\lhd$	$\delta_{as} N\lhd$				
IIa	138[†]	1613	1521	1347	865	1220	896		$C_{17}H_{15}N_3O_2$		76
IIb	134—135	1618	1523	1353	866	1225	891	13,8	$C_{18}H_{17}N_3O_2$	13,7	48
IIc	138	1612	1520	1348	862	1220	890	12,8	$C_{18}H_{17}N_3O_3$	13,0	52
IId	143—144	1624	1524	1348	864	1230	882	12,9	$C_{17}H_{14}ClN_3O_2$	12,8	80
IIe	138	1617	1518	1343	865	1221	890	11,5	$C_{17}H_{14}BrN_3O_2$	11,4	86
IIf	158	1620	1524	1330—1355	864	1221	895	16,5	$C_{17}H_{14}N_4O_4$	16,6	85
IIg	144	1620	1523	1349	867	1222	889	11,5	$C_{23}H_{19}N_3O_2$	11,4	53
IIa—HCl	128—131	1649	1523	1351	859	1241	866	13,4	$C_{17}H_{15}N_3O_2$—HCl	13,2	88

[†] According to the data in [2], this compound has mp 137-140°C.

As expected, electron-acceptor substituents in the aroyl fragment of I facilitate this conversion; this is manifested in the increase in the yields of the reaction products (Table 1).

Like aziridino[1,2-a]quinoxalines [1, 2], the colorless crystals of II under the influence of sunlight undergo an instantaneous change in color to blue-violet. The reverse process — dark decolorization of the photocolored form of II — occurs considerably more slowly (10-15 h). No photochromic transformations of II in solution at room temperature are observed. In contrast to aziridinoquinoxalines, thermochromism of toluene solutions at 100°C is not observed for bicyclic II.

Structure II was confirmed by the results of elementary analysis and data from the IR, PMR, and mass spectra. It is apparent from the data in Table 1 that the region of absorption of the stretching vibrations of the C=N group is 1612-1624 cm^{-1}, i.e., $\nu_{C=N}$ of II experience a pronounced low-frequency shift (up to 40 cm^{-1}) as compared with "open" azomethines (compare IIa with N-benzalmethylamine [3] with a band at 1654 cm^{-1}). This shift is undoubtedly due to compression of the azastyryl fragment in IIa. It is also interesting to note that even greater disparity in the $\nu_{C=N}$ values (up to 60 cm^{-1}) is observed when the data in Table 1 are compared with the analogous results for Δ^1-tetrahydropiperidines [4]. The increase in $\nu_{C=N}$ is due to the contribution of the electronic effect of the phenyl group conjugated with the C=N group.

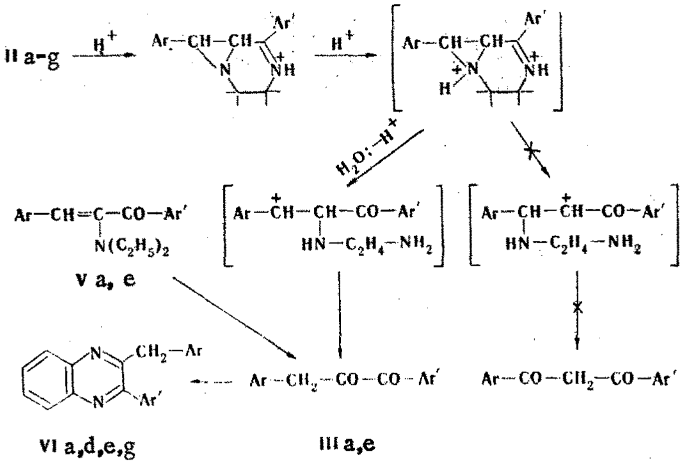
The skeletal vibrations of the ethyleneimine ring in the IR spectra of II are found at 1220-1230 and 882-895 cm^{-1}. The increase in the $\delta_s N\lhd$ and $\delta_{as} N\lhd$ values on passing from ethyleneimine itself (1214, 856 cm^{-1}) [5] is characteristic for N-alkyl-substituted aziridines and is associated with a change in the hybridization of the electron clouds of nitrogen because of steric effects [5].

The dimethylene bridge present in II is displayed in the IR spectra in the form of a doublet of symmetrical and asymmetrical ν_{CH_2} vibrations (2864-2875 and 2930-2948 cm^{-1}) and by the deformation scissors vibrations of the CH_2 group at 1435-1454 cm^{-1}.

Only doublet signals of the 6,7 protons of 1,4-diazobicyclo[4.1.0]hepta-4-ene system, which are located at, respectively, 3.0 and 3.5 ppm, can be reliably isolated in the PMR spectra in the region of aliphatic protons for IIa; the small spin—spin coupling constant (3 Hz) attests to the mutual transoid orientation of the protons in the 6 and 7 positions.

The following signals are observed in the mass spectrum of IIa: the molecular ion, m/e 293, 16%; $(M-1)^+$, m/e 292, 15%; $(C_6H_5CN)^+$, m/e 103, 100%; $C_6H_5^+$, m/e 77, 64%. These signals are also in agreement with the proposed structure of the compound.

The instability of azomethines in acidic media is well known. This type of behavior in the presence of acids is also characteristic for aziridines [8]. It seemed of interest to investigate the products of acidolysis of II, in which both acidophilic groups are present. It was found that although protonation does occur under relatively mild conditions (0.1 ml of concentrated HCl per 15 ml of a $2 \cdot 10^{-4}$ M alcohol solution if IIa at 20°C), it is not accompanied by more profound processes. For example, an acidified alcohol solution of IIa can be found unchanged after several days; neutralization of the solution leads to starting IIa. The formation of the only acidolysis product — 1,3-diarylpropane-1,2-dione (III) — is observed in concentrated H_2SO_4. It seemed of interest to prove the structure of compounds of the III type by alternative synthesis. Diketones of this type can be obtained in the action of alcoholic alkali on chalcone oxides IV [9]. However, we isolated only trace amounts of α-diketones (in the form of quinoxaline derivatives) from the reaction products. The reactions in this case is evidently complicated by other processes, as noted in [10]. The synthesis of the α-diketones was therefore accomplished from α-diethylaminochalcones V [11]. The diketones,* which were obtained by independent methods, gave identical quinoxaline derivatives VI on reaction with o-phenylenediamine. These results enabled us to present the following scheme for the transformations:



We will demonstrate below that the primary protonation center is the nitrogen atom of the ketimine group of IIa-g. However, protonation of the "aziridine" nitrogen atom probably also occurs in strongly acidic media, and it is precisely this process that makes the system unstable and facilitates its subsequent conversion.

As demonstrated by Cromwell [12] in the case of aziridinyl ketones, the intermediate formation of an aziridine salt in the presence of an acid leads to salts of 2-chloro-3-amino- or 3-chloro-2-amino-1-propanes, which are precursors of 1,3- and 1,2-diketones. The fact that only one product (1,2-diones) is obtained in our case is probably a consequence of the geometrical peculiarities of the rigid configuration of the starting II molecule, in which orientation of the p-nitrophenyl group in the aziridine ring is realized. This assumption is in agreement with the data in [8], in which it was shown that trans-aziridinyl ketones primarily form α-amino derivatives in hydrochloric acid media. This conclusion is confirmed even more unambiguously by the behavior of trans-2-(4'-nitrophenyl)-3-benzoylaziridine in concentrated sulfuric acid [2] (only the corresponding 1,2-dione was also isolated).

An important question for understanding the peculiarities of the chemical behavior of II is the determination of the site of primary protonation. A study of the IR spectra of the hydrochlorides of IIa and 4-phenyl-5-(4'-nitrophenyl)-2,2-dimethyl-1,3-diazabicyclo-[1.3.0]hexa-3-ene (VII) [13], which we obtained by passing dry HCl through solutions of bases IIa and VII in absolute ether, shows that the frequencies associated with the aziridine ring remain unchanged, whereas the $\nu_{C=N}$ frequencies increase regularly (Table 1). This confirms the assumption expressed above regarding the higher basicity of the nitrogen atom of the azomethine group in II. One can arrive at the same conclusion on the basis of the results of Heine and co-workers [14], who obtained the tetrafluoroborate of the N-methyl derivative of VII, in the reduction product of which the position of the methyl group was accurately established.

It is interesting to note that both of the hydrochlorides that we obtained display photochromic properties in the solid phase; however, in contrast to the bases, which are blue in light, the photoinduced form of the salts is red. This is undoubtedly due to the different distribution of the electron density in the dipolar ions that are proposed for an explanation of the photochromism of bicyclic compounds of the VII type [15].

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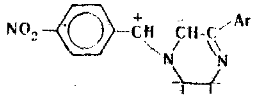
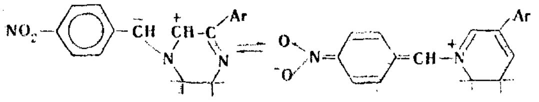
*These compounds probably exist in the enol form, since the following bands are observed in the IR spectrum of IIIa (KBr pellet): 3370 (OH), 1663 (C=O), and 1637 cm^{-1} (C=C). The position and form (a narrow intense signal) of the band attests to the presence of a strong intramolecular hydrogen bond in the enol.

Protonation of the nitrogen atom of the ketimine group should stabilize structure A, while structure B corresponds to the bases. The correctness of this assignment is confirmed, in our opinion, by the fact that bicyclic compounds of the VII type that do not contain a nitro group are also red (a similar pattern is also observed for the m-nitro derivatives of VII) [13]. A conjugated nitro group (in the para position of the 5-phenyl group of VII) promotes the distribution of the charges in the criterion that corresponds to the longer conjugation chain. Thus protonation of the azomethine group has a complete leveling effect on the stabilizing influence of the nitro group in structure B.


A


B

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were measured with a YaMR-5535 spectrometer at 40 MHz and 30°C with tetramethylsilane as the internal standard. The mass spectra were measured with an MAT-112 spectrometer.

5-(4'-Bromophenyl)-6-(4"-nitrophenyl)-1,4-diazabicyclo[4.1.0]hepta-4-ene (IIe). A 2.5-ml sample of ethylenediamine, which had been dried and distilled over KOH, and 10 ml of N,N-dimethylbenzylamine were added to a suspension of 12.0 g (0.025 mole) of Ie in 500 ml of methanol, and the mixture was refluxed until IIe began to precipitate. The mixture was then cooled and allowed to stand in the dark at 10°C for 2 days. The product was removed by filtration and washed liberally on the filter with 50% aqueous methanol to give 4.6 g of IIe with mp 136-137°C. An additional amount of a more impure product with mp 134°C was obtained by removing the solvent from the filtrate. The overall yield was 76%.

Crystallization from $CHCl_3-CH_3OH$ (1:3) gave pale-yellow needles with mp 138°C.

trans-2-(4'-Bromobenzoyl)-3-(4"-nitrophenyl)oxirane (IVe). A 5-ml sample of 40% NaOH solution and 4 ml of 30% H_2O_2 were added dropwise and alternately to a solution of 1.4 g (4.2 mmole) of trans-4-nitro-4'-bromochalcone in 25 ml of dioxane, during which the temperature of the solution rose to 35-45°C, and a copious gelatinous precipitate of percarbonates began to form. The reaction mixture was cooled with water and allowed to stand with periodic stirring for 1 h. Stirring was then continued, finely crushed ice was added, the solution was acidified to pH 4 with acetic acid, and the resulting oxide was removed by filtration. The yield was 1.19 g (82%)

Recrystallization from $CH_3OH-C_6H_6$ gave yellowish crystals with mp 164°C. IR spectrum: 1688 (C=O); 1525, 1346 cm^{-1} (NO_2). Found: N 4.1%. $C_{15}H_{10}BrNO_4$. Calculated: N 4.0%.

Oxiranes IVd, g were similarly obtained. Oxirane IVd had mp 159°C. IR spectrum: 1694 (C=O); 1528, 1349 cm^{-1} (NO_2). Found: N 4.5%. $C_{15}H_{10}ClNO_4$. Calculated: N 4.6%. Oxirane IVg had mp 151°C. IR spectrum: 1690 (C=O); 1533, 1351 cm^{-1} (NO_2). Found: N 4.1%. $C_{11}H_{15}NO_4$. Calculated: N 4.1%.

1-(4'-Bromophenyl)-3-(4"-nitrophenyl)-2-diethylamino-2-propen-1-one (Ve). A 3.4-g (12.5 mmole) sample of diethylamine was added to a cooled (to 0°C) suspension of 6.0 g (12.5 mmole) of 4-nitro-4'-bromochalcone dibromide in 75 ml of methanol, and the mixture was stirred at 0°C for 1.5 h, after which it was allowed to stand at room temperature with constant stirring for 2 days. The precipitated orange-red crystals of Ve were removed by filtration and crystallized from alcohol to give a product with mp 129°C. IR spectrum: 1675 (C=O); 1569 (C=C); 1558, 1325 cm^{-1} (NO_2). Found: N 7.1%. $C_{19}H_{19}BrN_2O_3$. Calculated: N 6.9%.

1-(4'-Bromophenyl)-3-(4"-nitrophenyl)propane-1,2-dione (IIIe). A) A 10-ml sample of cooled concentrated sulfuric acid was added with constant stirring to 1.50 g (0.041 mole) of IIe. After 15 min, the starting compound dissolved, and the yellow sulfuric acid solution was poured over 200 g of crushed ice. The mixture was allowed to stand at 20°C overnight, after which it was filtered. Crystallization of the precipitate from 80% aqueous methanol gave 1.22 g (86%) of golden-yellow crystal with mp 139-141°C. IR spectrum: 1653 (C=O); 1630 (C=C); 1528, 1330-1345 (NO_2); 3373 cm^{-1} (OH). Found: Br 23.1; N 3.9%. $C_{15}H_{10}BrNO_4$. Calculated: Br 23.0; N 4.0%.

B) A 0.38-g (0.95 mmole) sample of Ve was refluxed for 7 h with 30 ml of 15% H_2SO_4, after which the mixture was cooled, and diketone IIIe was removed by filtration to give 0.26 g (82%) of product. Recrystallization gave a product that was completely identical to the product obtained by method A.

2-(4'-Bromophenyl)-3-(4"-nitrobenzyl)quinoxaline (VIe). Compound VIe was obtained in quantitative yield by heating methanol solutions of equimolar amounts of IIIe and o-phenylenediamine. Recrystallization from methanol gave silky white crystals with mp 172°C. IR spectrum: 2930, 2855, 1460 (CH_3); 1527, 1347 cm^{-1} (NO_2). Found: N 10.1%. $C_{21}H_{14}BrN_3O_2$. Calculated: N 10.0%.

The following compounds were similarly obtained. Compound VIa had mp 123°C (mp 122-123°C [10]). IR spectrum: 2930, 2860, 1465 (CH_2); 1524, 1350 cm^{-1} (NO_2). Compound VId had mp 158-159°C. IR spectrum: 2930, 2852, 1487 (CH_2); 1522, 1349 cm^{-1} (NO_2). Found: N 10.9%. $C_{21}H_{14}ClN_3O_2$. Calculated: N 10.8%. Compound VIg had mp 144°C. IR spectrum: 2930, 2856, 1463 (CH_2); 1518, 1351 cm^{-1} (NO_2). Found: N 10.2%. $C_{27}H_{19}N_3O_2$. Calculated: N 10.1%.

LITERATURE CITED

1. V. D. Orlov, F. G. Yaremenko, N. N. Kolos, and V. F. Lavrushin, Dokl. Akad. Nauk Ukr. SSR, Ser. B, No. 3, 247 (1978).
2. H. W. Heine and R. P. Henzel, J. Org. Chem., 34, 171 (1969).
3. L. Bellamy, New Data on the IR Spectra of Complex Molecules [Russian translation], Mir, Moscow (1971), p. 59.
4. A. Katritzky (ed.), Physical Methods in the Chemistry of Heterocyclic Compounds, Academic Press (1963).
5. É. É. Liepin'sh, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 9, 32 (1976).
6. H. T. Hobbmann, G. E. Evans, and G. Glockler, J. Am. Chem. Soc., 37, 3028 (1951).
7. R. R. Shagiddulin and N. P. Grechkin, Khim. Geterotsikl. Soedin., No. 2, 305 (1967).
8. N. H. Cromwell and R. J. Wankel, J. Am. Chem. Soc., 71, 711 (1949).
9. H. Jorlander, Ber., 50, 406 (1917).
10. R. P. Barnes, J. H. Graham, and M. A. S. Qureshi, J. Org. Chem., 28, 2890 (1963).
11. N. H. Cromwell and G. D. Mecser, J. Am. Chem. Soc., 79, 3873 (1957).
12. N. H. Cromwell, Rec. Chem. Progr., 19, 215 (1958).
13. H. W. Heine, R. H. Weese, R. A. Cooper, and A. J. Durbetaki, J. Org. Chem., 32, 2708 (1967).
14. H. W. Heine, T. A. Newton, G. J. Blosick, K. C. Irving, C. Meyer, and G. B. Corocoran, J. Org. Chem., 38, 651 (1973).
15. T. Do Minh and A. M. Trozzolo, J. Am. Chem. Soc., 94, 4046 (1972).