TABLE 3. N-(1-Benzyl-2-aziridinyl-carbonyl)amino Acid Methyl Esters (IVa-h)

Compound	R_f	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
IVa	0,48	62,5	6,7	10,9	$C_{13}H_{16}N_2O_3$	62,9	6,5	11,3	10
IVb	0,75	63,7	6,8	10,4	$C_{14}H_{18}N_2O_3$	64,1	6,9	10,7	15
IVc	0,72	65,8	7,5	10,1	$C_{16}H_{22}N_2O_3$	66,2	7,6	9,7	12
IVd	0,60	70,8	6,3	8,1	$C_{20}H_{22}N_2O_3$	71,0	6,5	8,3	20
IVe	0,57	67,5	6,1	7,5	$C_{20}H_{22}N_2O_4$	67,8	6,2	7,9	18
IVf	0,55	59,1	7,2	8,8	$C_{16}H_{22}N_2O_3S$	59,6	6,8	8,7	14
IVg	0,43	59,6	6,5	8,8	$C_{16}H_{20}N_2O_5$	60,0	6,3	8,8	15
IVh	0,37	60,7	6,7	8,0	$C_{17}H_{22}N_2O_5$	61,1	6,6	8,4	10

was added to the solution of azide II obtained by the method described above, and the mixture was allowed to stand at 0°C for 12 h. The solvent was removed by distillation, and the residue was transferred to a preprepared plate with silica gel (Merck) and chromatographed in an ether—ethyl acetate system (1:1).

LITERATURE CITED

1. S. Patai (editor), The Chemistry of the Azido Group, Interscience Publ., London—New York (1971), p. 503.
2. N. H. Cromwell and R. I. Wankel, J. Am. Chem. Soc., 71, 711 (1949).
3. Y. Honzl and Y. Ridinger, Collect. Czech. Chem. Commun., 26, 2333 (1961).
4. F. L. Scott and M. T. Scott, J. Am. Chem. Soc., 79, 6077 (1957).
5. A. V. Eremeev, F. D. Polyak, and T. V. Stol'tser, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 3, 355 (1979).
6. J. Brauer (editor), Handbuch der Präparativen Anorganischen Chemie, Enke, Stuttgart (1954), p. 387.

SYNTHESIS OF cis-1-METHYL-2-ARYL-3-AROYLAZIRIDINES

I. G. Tishchenko, O. N. Bubel',
and V. A. Konovalov

UDC 547.717.07:541.634

trans-1-Methyl-2-aryl-3-aroylaziridines readily undergo epimerization to give the corresponding cis isomers in high yields in the presence of catalytic amounts of quaternary ammonium bases (trimethylbenzylammonium or triethylmethylammonium hydroxide). The structures of the compounds obtained were established on the basis of the IR and PMR spectra and the results of elementary analysis.

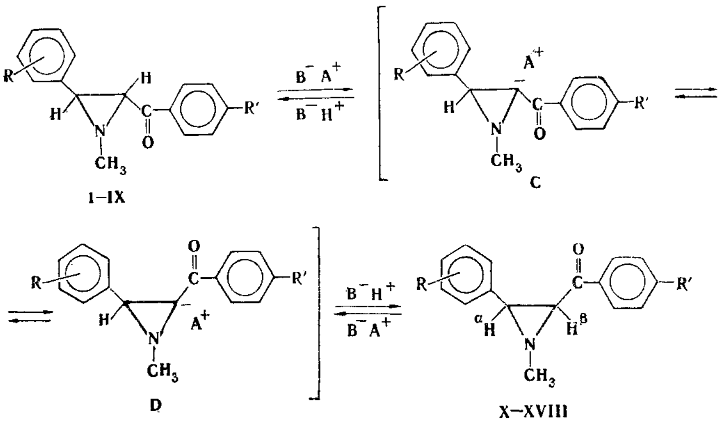
3-Aroylaziridines are promising substances for the preparation of various nitrogen-containing polyfunctional organic compounds. The preparative methods for the synthesis of trans-3-aroylaziridines have undergone a great deal of development [1, 2], while very little study has been devoted to the development of methods for the preparation of the cis derivatives of aroylaziridines. The isomerization of trans-3-aroylaziridines in the presence of bases [3] evidently may serve as the most practicable method for the synthesis of cis-3-aroylaziridines. However, in the known examples of isomerization [3, 4] the cis isomers are obtained in 40-50% yields, and the reaction time reaches 7-8 days. Sodium methoxide and potassium tert-butoxide have been used as the bases. The solvents were methanol and tert-butyl alcohol, as well as alcohol—tetrahydrofuran (THF) and benzene—ether solvent mixtures.

According to [4], the isomerization of trans-3-aroylaziridines in the presence of bases to the thermodynamically more stable [4] cis isomers proceeds through a step involving the

---

V. I. Lenin Belorussian State University, Minsk 220080. Translated from Khimiya Geterotsilicheskikh Soedinenii, No. 10, pp. 1353-1355, October, 1980. Original article submitted December 18, 1979; revision submitted March 24, 1980.

0009-3122/80/1610-1025$07.50



I, X R=H, R′=H; II, XI R=p-CH$_3$O, R′=H; III, XII R=p-CH$_3$, R′=H; IV, XIII R=p-Cl, R′=H; V, XIV R=p-Br, R′=H; VI, XV R=m-NO$_2$, R′=H; VII, XVI R=H, R′=CH$_3$O; VIII, XVII R=H, R′=Cl; IX, XVIII R=H, R′=Br

formation of carbanion C at the α-carbon atom of the aziridine ring with respect to the carbonyl group. The electron pair of carbanion C is located on the same side of the plane of the ring as the unshared electron pair of the nitrogen atom, as a consequence of which the carbanion is unstable and is rapidly converted by the addition of a proton to the starting trans-3-aroylaziridine or undergoes isomerization more slowly to cis-carbanion E. In the case of catalysis with sodium methoxide equilibrium (cis/trans 77:23) is reached only after 168 h [4], evidently as a consequence of the inefficient stabilization of the resulting C carbanion. The C anion is a soft base [5]. According to Pearson's concept [5], the particles that are necessary for its more effective stabilization as a gegenion are not alkali metal cations (hard acids) but rather soft acids, the lower vacant orbitals of which are located in a higher energy level as compared with the energy levels of alkali metal cations. It is known [6] that quaternary ammonium bases (QAB) are excellent catalysts of reactions that proceed through the formation of carbanions. Precisely quaternary ammonium bases constitute one case of "symbiosis" relative to a soft acid (Alk$_4$N$^+$) and a hard base (OH$^-$).

Our use of quaternary ammonium bases as catalysts for the isomerization of trans-3-aroylaziridines demonstrated their high effectiveness. Thus, trans-1-methyl-2-aryl-3-aroylaziridines (I-IX) readily undergo isomerization at room temperature in the presence of catalytic amounts of 15% aqueous solutions of trimethylbenzylammonium or triethylmethylammonium hydroxide in acetone containing 15-20% methanol to the corresponding cis-1-methyl-2-aryl-3-aroylaziridines (X-XVIII) in 65-85% yields (Table 1). After 8-12 h, the ratio of the isomers (cis/trans) reaches 83:17 and subsequently remains unchanged. The completely isomerized trans-1-methyl-2-(m-nitrophenyl)-3-benzoylaziridine constitutes an exception; this is associated with the low solubility of the cis isomer. It is characteristic that the rate of isomerization decreases in both pure methanol and pure acetone. In the first case the decrease in the rate is evidently due to solvation effects, whereas in the second case it is due to a decrease in the concentration of the proton donor.

Intense absorption bands of the stretching vibrations of the carbonyl group (1675-1688 cm^{-1}) are observed in the IR spectra of cis-aziridines X-XVIII; the high-frequency wing has a higher intensity than the absorption band of the carbonyl group of the trans-aziridines, the low-frequency wing of which has a higher intensity. The stretching and deformation vibrations of the bonds of the aromatic rings are observed at 3075, 3040, 1600, and 1480 cm^{-1}, while the absorption bands at 850 and 1230 cm^{-1} indicate the presence of an aziridine system [7].

The PMR spectra of cis-aziridines X-XVIII are presented in Table 2. The spin–spin coupling constants of 5.8-6.2 Hz (2.6-2.8 Hz for the trans isomer [8]) provide evidence for the configuration of X-XVIII. The assignment of the signals of the H$_\alpha$ and H$_\beta$ protons in the PMR spectra was made on the basis of deuterium exchange experiments.

EXPERIMENTAL

The course of the reactions and the individuality of the compounds were monitored by thin-layer chromatography (TLC) on Silufol plates [ether–hexane (3:1)]. The PMR spectra of

TABLE 1. Physicochemical Constants of cis-1-Methyl-2-aryl-3-aroylaziridines (X-XVIII)

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
X	86	80,9	6,2	5,9	$C_{16}H_{15}ON$	81,0	6,1	5,9	68
XI	106	76,4	6,7	5,4	$C_{17}H_{17}O_2N$	76,3	6,4	5,6	66
XII	97	81,0	6,9	5,4	$C_{17}H_{17}ON$	81,3	6,8	5,6	70
XIII	94	70,7	5,4	5,1	$C_{16}H_{14}ONCl$	70,8	5,2	5,2	72
XIV	119	61,0	4,5	4,4	$C_{16}H_{14}ONBr$	60,7	4,4	4,4	74
XV	140	64,6	5,0	9,6	$C_{16}H_{14}O_3N_2$	64,4	4,8	9,3	87
XVI	84	76,3	6,6	5,3	$C_{17}H_{17}O_2N$	76,3	6,4	5,6	65
XVII	87	71,0	5,4	5,1	$C_{16}H_{14}ONCl$	70,8	5,2	5,2	69
XVIII	84	60,6	4,7	4,5	$C_{16}H_{14}ONBr$	60,7	4,4	4,4	72

TABLE 2. PMR Spectra of cis-1-Methyl-2-aryl-3-aroylaziridines (X-XVIII)

Compound	Chemical shift, δ, ppm				J_{H-H}, Hz
	$N-CH_3$	H_β	H_α	H_{arom}	
X	2,25	2,44	2,56	6,60—7,78	5,8
XI	2,53	2,77	2,90	6,50—7,82	6,2
XII	2,51	2,73	2,87	6,73—7,86	6,2
XIII	2,53	2,77	2,94	6,98—7,84	6,0
XIV	2,54	2,79	2,97	6,97—7,83	5,8
XV	2,59	3,04	3,20	7,19—8,25	6,0
XVI	2,49	2,72	2,82	6,62—7,87	6,8
XVII	2,54	2,78	2,85	6,94—7,86	5,8
XVIII	2,52	2,77	2,87	6,90—7,80	6,0

10% solution in CCl_4 were recorded with a BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of 0.1 M solutions in CCl_4 were recorded with a UR-20 spectrometer.

The trans-1-methyl-2-aryl-3-aroylaziridines were obtained by reaction of chalcones with an iodine—amine complex by the method in [9].

cis-1-Methyl-2-aryl-3-aroylaziridines (X-XVIII). A 0.1-mole sample of trans-1-methyl-2-aryl-3-aroylaziridine was dissolved in a mixture of 200-300 ml of acetone containing 10-20% methanol, 0.01 mole of a 15% aqueous solution of triethylbenzylammonium or triethylammonium hydroxide (based on 100% of the quaternary ammonium base) was added, and the mixture was allowed to stand overnight. The solvents were removed by distillation at reduced pressure, the residue was dissolved in ether, and the ether solution was washed with three portions of water. The extract was dried with potassium carbonate, the ether was evaporated, and the product was crystallized from hexane—isopropyl alcohol. The compounds were obtained in 65-87% yields.

Deuterium-Exchange Experiment. A 0.1-g sample of cis-3-aroylaziridine and 0.03 g of sodium methoxide were dissolved in 0.1 ml of D-6 deuteromethanol in an ampul, and the mixture was allowed to stand at room temperature. After 10 min, the substrate had undergone 90% deuterium exchange. The exchange was monitored by PMR spectroscopy.

LITERATURE CITED

1. P. L. Southwick and W. L. Walsh, J. Am. Chem. Soc., 77, 405 (1955).
2. I. G. Tishchenko, O. N. Bubel', V. A. Konovalov, and N. M. Fedoseeva, Vestn. Beloruss. Gos. Univ., Ser. 2, 27 (1979).
3. R. E. Lutz and A. B. Turner, J. Org. Chem., 33, 516 (1968).
4. P. Tarburton, A. Chung, R. C. Badger, and N. H. Cromwell, J. Heterocycl. Chem., 13, 295 (1976).
5. G. Klopman, Chemical Reactivity and Reaction Paths, New York (1974).
6. L. Fieser and M. Fieser, Reagents for Organic Synthesis, Vol. 3, Wiley, New York (1973).
7. P. A. Gembitskii, D. S. Zhuk, and V. A. Kargin, The Chemistry of Ethyleneimine [in Russian], Nauka, Moscow (1966), p. 51.
8. N. H. Cromwell, J. Heterocycl. Chem., 14, No. 7, 203 (1977).