dinium and thiazoloquinolinium oxides II and IV leads to deepening of their coloration. As in the case of the starting compounds, a greater bathochromic shift of the band obtained experimentally as compared with the theoretical estimate ($\Delta\lambda$ 28 nm) is observed for product VI; the latter value is somewhat lower than in the case of oxide IV ($\Delta\lambda$ 37 nm), which can probably be explained by the smaller decrease in the order of the C_1—C_2 bond on passing to the excited state for VI ($\Delta p_{1,2} = -0.2031$).

Thus the quantum-chemical analysis of thiazolopyridinium derivatives carried out in this paper makes it possible to explain the difference in their coloration and reactivities with respect to electrophiiic reagents.

LITERATURE CITED

1. L. T. Gorb, A. D. Kachkovskii, N. N. Romanov, I. S. Shpileva, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 5, 621 (1980).
2. A. R. Katritzky and A. V. Boulton, Advances in Heterocyclic Chemistry, Vol. 19, Academic Press, New York—San Francisco—London (1976), p. 3.
3. P. B. Talukdar, S. K. Sengupta, and A. K. Datta, Indian J. Chem., 16B, 678 (1978).
4. Yu. A. Kruglyak, G. G. Dyadyusha, V. A. Kuprievich, A. M. Podol'skaya, and G. I. Kogan, Methods for the Calculation of the Electronic Structures and Spectra of Molecules [in Russian], Naukova Dumka (1969), p. 175.
5. I. Fabian, R. Zahradnic, and Z. Wizz, Tech. Univ. (Dresden), 26, 315 (1977).
6. N. Mataga and K. Nishimoto, Z. Phys. Chem., N. F., 13, 140 (1953).
7. A. Gordon and R. Ford, The Chemist's Companion, Wiley (1973).
8. L. T. Gorb, N. N. Romanov, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 10, 1343 (1979).
9. S. F. Mason, in: Physical Methods in the Chemistry of Heterocyclic Compounds, A. R. M. Katritzky, ed., Academic Press (1963).
10. L. T. Gorb, E. D. Sych, A. I. Tolmachev, and I. S. Shpileva, Khim. Geterotsikl. Soedin., No. 8, 1066 (1979).
11. L. T. Gorb, N. N. Romanov, E. D. Sych, and A. I. Tolmachev, Dokl. Akad. Nauk Ukr. SSR, No. 10, 895 (1978).

FORMATION OF IMIDAZOLE SYSTEMS IN THE REACTIONS OF 2,2-DIMETHYL-3-PHENYLAZIRINE WITH AMIDINES, ETHYL CARBAMATE, AND RHODANAMINE

A. V. Eremeev, R. S. El'kinson
É. É. Liepin'sh, and V. A. Imuns

UDC 547.298.5.495.1:546.268.5

The reactions of 2,2-dimethyl-3-phenylazirine with guanidine, guanylurea, formamidinium acetate, ethyl carbamate, and rhodanamine lead to substituted imidazoles, 2-imidazolidone, and imidazolidine-2-thione. It was established experimentally that the initial process is nucleophilic addition of alcohol to the azirine, after which the resulting 3-alkoxy-2,2-dimethyl-3-phenylaziridine reacts with the amine component to give the corresponding imidazole derivative.

It is known the ethyl ester of carbazic acid reacts with 3-dimethylamino-2,2-dimethyl-2H-azirine to give 4,5-dihydro-1,2,4-triazine-3(2H)-one [1]. No information regarding the reaction of 2H-azirine with amines, ethyl carbamate, and rhodanamine is available in the literature.

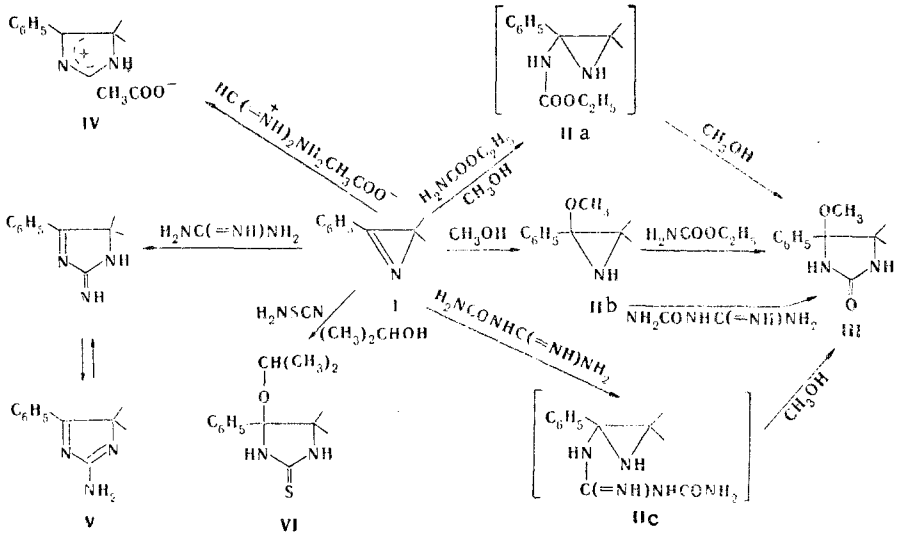
We have investigated the reactions of 2,2-dimethyl-3-phenylazirine (I) with ethyl carbamate (urethane), formamidinium acetate, guanylurea, guanidine, and rhodanamine.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.

Translated from Khimiya Geterotsiklicheskikh Soedinenni, No. 12, pp. 1624-1626, December, 1980. Original article submitted March 20, 1980.

0009-3122/80/1612-1226$07.50

NMR spectra of III obtained by the reaction of azirine I with ethyl carbamate in ntains two singlets of NH groups at 7.92 and 6.59 ppm and singlets of protons of ing and a methoxy group. A singlet of the carbon atom of a C=O group at 161.5 rved in its ^{13}C NMR spectrum. The presence of nonequivalent resonance signals groups in the ^{1}H and ^{13}C NMR spectra constitutes evidence for the cyclic struc-. The band of C=O stretching vibrations (1715 cm^{-1}) that is characteristic for l group in five-membered cyclic ureides is observed in the vibrational spectra the basis of the spectra and analytical data it may be assumed that 4-methoxy-l-4-phenyl-2-imidazolidone (III) is formed in the reaction of azirine I with ethyl The formation of imidazolidone III is in agreement with the data in [1], which e intermediate formation of aziridine IIa. However, one cannot exclude the possi-the first step in the reaction is the formation of alkoxyaziridine IIb, the sub-ction of which with urethane leads to imidazolidone III.



ine and imidazolidone III were isolated during a study of the reaction of azirine ylurea in methanol. The formation of these compounds can be explained either by for intermediate aziridine IIc to undergo isomerization to an ylid system [2] with rearrangement with the splitting out of guanidine or by the probable reaction of with alkoxyaziridine IIb, as a result of which imidazolidone III and guanidine are confirmed the latter assumption experimentally. Thus guanidine and imidazolidone olated in the reaction of 3-methoxy-2,2-dimethyl-3-phenylaziridine, obtained by in [3], with guanylurea in methanol.

action of azirine I with formamidinium acetate takes place with the formation of rational spectrum of which contains bands of vibrations of the C=N bond (1640, and the CH_3COO^- ion (1550 and 1395 cm^{-1}), as well as a broad band of stretching of an NH group at 3300 cm^{-1}. A singlet of gem-CH_3 groups and a singlet of an proton (8.70 ppm) are observed in the PMR spectrum of IV. The appearance of a of stretching vibrations of an NH group in the region of a free amino group (3300 r than in the ammonium region makes it possible to assume that the positive charge lized on the nitrogen atoms but rather is distributed over the system of bonds in basis of the data presented above, as well as the analytical data, it may be con-5,5-dimethyl-4-phenylimidazolinium acetate (IV) is formed in the reaction of ith formamidinium acetate.

nglet of gem-CH_3 groups, a broad singlet of an NH group (with an intensity of two s), and a multiplet of phenyl protons are observed in the PMR spectrum of V ob-ne reaction of azirine I with guanidine, while bands of C=N (1680 cm^{-1}), NH_2 270 cm^{-1}), and imino (3485 cm^{-1}) groups are observed in the vibrational spectrum. ssumed that tautomers, viz., 2-imino-5,5-dimethyl-4-phenyl-3-imidazoline and -dimethyl-4-phenylimidazole (V), are formed as a result of the reaction of azirine ldine.

opoxy-5,5-dimethyl-4-phenylimidazolidine-2-thione (VI) was isolated in the reac-rine I with rhodanamine in isopropyl alcohol. Signals of nonequivalent gem-CH_3

TABLE 1. Physicochemical Characteristics of III-VI

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
III	180—181	65,1	7,1	12,5	$C_{12}H_{16}N_2O_2$	65,4	7,3	12,7	56
IV	110—111	66,9	6,6	11,8	$C_{13}H_{16}N_2O$	67,2	6,9	12,1	64
V	174—175	70,2	6,7	22,1	$C_{11}H_{13}N_3$	70,6	6,9	22,4	47
VI	171—172	67,5	7,9	11,0	$C_{14}H_{20}N_2OS$*	67,7	8,1	11,3	74

*Found: S 12.7%. Calculated: S 12.9%.

groups are observed in its ^1H and ^{13}C spectra, and this constitutes evidence for its cyclic structure. Two broad singlets of NH groups (9.36 and 8.58 ppm) are also recorded in the ^1H NMR spectrum, and the ^{13}C spectrum contains a singlet at 180.9 ppm, which should be ascribed to the resonance of the carbon atom of the C=S bond (a band of stretching vibrations of a C=S bond is observed in the IR spectrum at 1550 cm^{-1}). A molecular ion of imidazolidinethione VI cannot be recorded in the mass spectrum of VI, but an ion with m/e 204 corresponding to a substituted 3-imidazoline-2-thione is observed. Splitting out of isopropyl alcohol probably occurs under the influence of electron impact, and 2-thio-5,5-dimethyl-4-phenyl-3-imidazoline-2-thione is formed.

The formation of imidazole derivatives in the reactions of azirine I with amidines, ethyl carbamate, and rhodanamine evidently occurs as a consequence of rearrangement of the intermediates, which is accompanied by the ejection of easily split out products.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in Nujol and hexachlorobutadiene were obtained with UR-20 and Specord spectrometers. The mass spectrum was recorded with an MS-905 spectrometer (70 eV). The ^1H NMR spectra of 5% solutions of the compounds were obtained with Perkin-Elmer R-12A (60 MHz) and Bruker WH-90 spectrometers with tetramethylsilane (TMS) as the internal standard. The ^{13}C NMR spectra were recorded with a Bruker WH-90 spectrometer. The chemical shifts were measured relative to TMS. The physicochemical characteristics of III-VI are presented in Table 1.

4-Methoxy-5,5-dimethyl-4-phenyl-2-imidazolidone (III). A solution of 3.7 g (0.03 mole) of ethyl carbamate in 10 ml of methanol was added to a solution of 4.7 g (0.03 mole) of azirine I [3] in 30 ml of methanol, and the mixture was stirred at 70°C for 3 h. The alcohol was removed by distillation, and the residue was recrystallized from petroleum ether to give 3.7 g (56%) of a product with mp 180-181°C. ^1H NMR spectrum (d_6-DMSO), δ: 0.54 and 1.23 (3H and 3H, s, C—CH_3), 2.90 (3H, s, OCH_3), 6.59 (1H, s, NH), 7.38 (5H, s, C_6H_5), and 7.92 ppm (1H, s, NH). ^{13}C NMR spectrum (d_6-DMSO), δ: 21.7 and 28.7 (q,* CH_3), 50.6 (q, OCH_3), 62.7 (s, quaternary C), 96.1 (s, quaternary C), 128.4 (d, C_m), 129.3 (d, C_o and C_p), 138.2 (s, C_α), and 161.5 ppm (s, C=O).

Compounds IV and V were similarly obtained. The individuality of III-VI was confirmed by thin-layer chromatography (TLC).

5,5-Dimethyl-4-phenyl-3-imidazolinium Acetate (IV). ^1H NMR spectrum (d_6-DMSO), δ: 1.43 (6H, s, C—CH_3), 1.65 (3H, s, CH_3COO^-), 3.36 (1H, s, NH), 7.59 (3H, m, H_m and H_p), 7.96 (2H, m, H_o), and 8.70 ppm (1H, s, CH).

2-Imino-5,5-dimethyl-4-phenyl-3-imidazoline (V). ^1H NMR spectrum ($CDCl_3$), δ: 1.54 (6H, s, C—CH_3), 5.19 (2H, s, NH and C=NH), 7.56 (3H, m, H_m and H_p), and 8.10 ppm (2H, m, H_o).

4-Isopropoxy-5,5-dimethyl-4-phenylimidazolidine-2-thione (VI). A solution of 4.3 g (0.03 mole) of azirine I in 30 ml of isopropyl alcohol was added to a solution of 2 g (0.03 mole) of rhodanamine [4] in 250 ml of benzene, and the mixture was stirred at 70°C for 3 h. The solvent was removed by distillation, and the residue was recrystallized from ethanol to give 4.9 g (74%) of a product with mp 171-172°C. ^1H NMR spectrum (d_6-DMSO), δ: 0.47 and 1.27 (3H and 3H, s, C—CH_3), 0.87 and 1.05 (3H and 3H, d, J = 6 Hz, isopropyl CH_3), 3.49 (1H, septet, J = 6 Hz, CH), 7.38 (5H, s, C_6H_5), and 8.58 and 9.36 ppm (1H and 1H, s, NH). ^{13}C NMR

*The multiplicity of the signal in an off-resonance experiment is indicated.

spectrum (d_6-DMSO), δ: 19.3, 23.5, 24.6, 25.6 (q, CH_3); 65.2 (s, quaternary C); 66.5 (d, CH); 97.4 (s, quaternary C); 127.1 and 127.6 (d, C_o and C_m); 128.1 (d, C_p); 137.3 (s, C_α); 180.9 ppm (s, C=S).

LITERATURE CITED

1. H. Link, Helv. Chim. Acta, 61, 2419 (1978).
2. T. Nishiwaki and T. Saito, J. Chem. Soc., C, 2648 (1971).
3. R. F. Parcell, Chem. Ind., 33, 1396 (1963).
4. E. Schmitz and H. Strieger, J. Prakt. Chem., 312, 359 (1970).