(49%) of a product with mp 126-127°C. Found: C 44.5; H 5.0; Cl 10.2%. $C_{13}H_{17}ClSeO_4$. Calculated: C 44.3; H 4.8; Cl 10.1%. The mother liquor was washed with water, dried over Na_2SO_4, and distilled to remove the solvent. The oily residue was crystallized from CH_3OH to give 0.87 g (34%) of perhydroselenoxanthene (VI) with mp 62-63°C. Found: C 61.1; H 9.3%. $C_{13}H_{22}Se$. Calculated: C 60.7; H 8.6%.

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REACTIONS OF 2,2-DIMETHYL-3-PHENYLAZIRINE WITH CHLORIDES OF UNSATURATED AND AMINO-SUBSTITUTED ACIDS

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The reaction of 2,2-dimethyl-3-phenylazirine with N-phthalylglycine acid chloride gives initially N-acyl-3-chloroaziridine, which undergoes isomerization to a substituted 2-oxazoline and the corresponding keto amide. The reaction of 2,2-dimethyl-3-phenylazirine with the chlorides of crotonic, β-(2-furyl)acrylic, cinnamic, and phenylpropiolic acids in benzene at 20°C leads to 2,2-dimethylindoxyl and the corresponding unsaturated acid.

The literature contains extremely disparate data on the products of the reaction of 2H-azirines with acid chlorides. It has been established that substituted oxazoles [1-4,6-8], α,β-unsaturated N-acylamidines [5], N-acylaziridines [6], and the corresponding dichloro amides [7, 8] are formed.

We set out to study the reaction of 2,2-dimethyl-3-phenylazirine with the chlorides of amino acids in order to obtain compounds that contain aziridine and amino acid fragments, as well as to study the conditions for the preparation of N-acyl-2-haloaziridines for their subsequent conversion to 2-aminoaziridines. It also seemed of interest to investigate the reaction of 2,2-dimethyl-3-phenylazirine (I) with the chlorides of unsaturated acids, first, in view of the discrepancies in the literature data [4, 6], and second, because of the fact that the presence in the expected reaction products of multiple bonds makes it possible to assume the possibility of the preparation of polymeric compounds with an aziridine ring.

We studied the reaction of 2,2-dimethyl-3-phenylazirine with the chlorides of N-phthalylglycine and crotonic, β-(2-furyl)acrylic, cinnamic, and phenylpropiolic acids.

We found that 1-(N-phthalylglycyl)-3-chloro-2,2-dimethyl-3-phenylaziridine is formed in quantitative yield when equimolar amounts of 2,2-dimethyl-3-phenylazirine (I) and N-phthalylglycine acid chloride are simply stirred in benzene for 1.5 h. Bands of vibrations of a C=O bond at 1680, 1705, and 1730 cm^{-1} are observed in the IR spectrum of II, and a doublet of gem-CH_3 groups (1.08 and 1.77 ppm), signals of a system of the AB type from the protons of the methylene group (4.59 and 4.76 ppm), and multiplets of protons of phthalyl and phenyl groups are recorded in the PMR spectrum. When the reaction time is increased to 3.5 h, in the PMR spectrum of the isolated substance one observes, in addition to the

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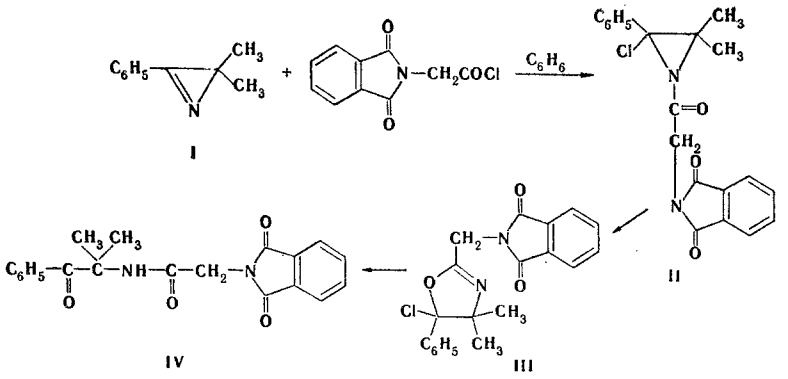
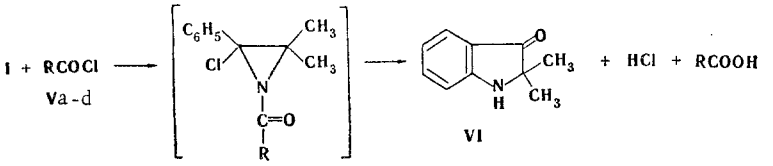
resonance signals of N-acylaziridine II, singlets of protons of methyl groups at 0.72 and 1.54 ppm (each with an intensity of 3H), as well as at 1.72 ppm (with an intensity of 6H); this probably constitutes evidence for the formation of the corresponding 2-oxazoline and keto amide [6]. Thus the isolated substance is a mixture of substituted N-acyl-3-chloroaziridine II, 2-oxazoline III, and keto amide IV in a ratio of 2:1:1, respectively.

Keto amide IV is formed in almost quantitative yield 5 h from the start of the reaction; characteristic absorption bands of carbonyl groups (1650 and 1680 cm^{-1} and 1720 and 1780 cm^{-1}) and stretching vibrations of an amide NH bond (3300, 3070 cm^{-1}) are observed in the IR spectrum of IV. The PMR spectrum of IV contains a broad singlet of protons of an NH group at 6.98 ppm, singlets of protons of a methylene group at 4.68 ppm, singlets of gem-CH_3 groups at 1.71 ppm (with an intensity of 6H), and multiplets of phenyl and phthalyl protons. Thus we have established that the reaction of 2,2-dimethyl-3-phenylazirine with N-phthalylglycine acid chloride leads to 1-(N-phthalylglycyl)-3-chloro-2,2-dimethyl-3-phenylaziridine (II), which is capable of undergoing isomerization very readily to the corresponding 2-oxazoline III and keto amide IV.



Compounds that are identical with respect to their analytical and spectral data were isolated in the reaction of azirine I with the chlorides of crotonic, β-(2-furyl)acrylic, cinnamic, and phenylpropiolic acids in benzene at 20°C. A band of stretching vibrations of a C=O bond (1680 cm^{-1}) and stretching vibrations of an NH group at 3470 cm^{-1}, which are characteristic for this sort of group in indoles, are present in the vibrational spectrum of the reaction product. A singlet of gem-CH_3 groups (1.76 ppm), multiplets of aromatic protons, and a broad singlet of protons of an NH group at 8.74 ppm are recorded in the ^1H NMR spectrum. A singlet that should be assigned to the resonance of the carbon atom of the C=O bond is observed in the ^{13}C NMR spectrum at 198.8 ppm. Consequently, it may be assumed that the spectroscopic and analytical data indicate the formation in the reactions of azirine I with the chlorides of crotonic, cinnamic, β-(2-furyl)acrylic, and phenylpropiolic acids (Va-d) of 2,2-dimethylindoxyl (VI), which was isolated in the form of the hydrochloride:



V a R=$C_6H_5C{\equiv}C$, b R=$CH_3CH{=}CH$, c R= 2-(2-furyl)vinyl, d R=$C_6H_5CH{=}CH$

The properties of the 2,2-dimethylindoxyl isolated in the free form correspond to the literature data [9, 10]. It is known that 2,2-disubstituted indoxyls readily undergo rearrangement to 3,3-disubstituted oxindoles in the presence of strong acids [11, 12]. The rearrangement of VI to the corresponding known 3,3-dimethyloxindole [13] that we accomplished also serves as proof for the 2,2-dimethylindoxyl (VI) structure. Substituted N-acyl-3-chloroaziridines [6] are evidently formed initially and then undergo hydrolysis under the isolation conditions to give the corresponding unsaturated acids. We confirmed this assumption experimentally. Thus, for example, in the reaction of azirine I with the chlorides of phenylpropiolic acid, in addition to indoxyl VI, we also isolated phenylpropiolic acid, the spectral characteristics and melting point of which are in agreement with the data in [14].

The results of our study of the conversion of the substituted 2-haloaziridines to the corresponding 2-aminoaziridines will be published in our future communications.

EXPERIMENTAL

The melting points of the substances obtained were determined with the microheating stage of a Boetius system. The IR spectra of the compounds in Nujol were obtained with UR-20 and Specord spectrometers. The ^1H NMR spectra of 5% solutions of the compounds were recorded with a Bruker WH-90 spectrometer with tetramethylsilane (TMS) as the internal standard. The ^{13}C NMR spectrum of VI was obtained with a Bruker WH-90 spectrometer (22.63 MHz) the chemical shifts were measured relative to TMS.

1-(N-Phthalylglycyl)-3-chloro-2,2-dimethyl-3-phenylaziridine (II). This compound, with mp 114-115°C, was obtained in 62% yield by the method in [6]. IR spectrum: 1730, 1706, and 1680 cm^{-1} (C=O). PMR spectrum ($CDCl_3$), δ: 1.08 and 1.77 (3H and 3H, s, CH_3); 4.59, 4.76 (2H, system of the AB type, CH_2); 7.45 (5H, m, C_6H_5); 7.98 ppm (4H, m, phthalyl). Found: 64.9; H 4.2; N 7.4%. $C_{20}H_{17}ClN_2O_3$. Calculated: C 65.1; H 4.6; N 7.6%.

2-(N-Phthalylglycyl)amino-2-methyl-1-phenyl-1-propanone (IV). This compound, with mp 208-210°C, was obtained in 71% yield by the method in [6]. IR spectrum: 1650-1730 (C=O); 3300, 3070 cm^{-1} (NH). PMR spectrum ($CDCl_3$), δ: 1.71 (6H, s, CH_3), 4.68 (2H, s, CH_2), 6.98 (1H, s, NH), 7.34 (3H, m, H_m and H_p), and 7.76 ppm (2H and 4H, m, H_o and phthalyl). Found: 68.3; H 4.8; N 7.8%. $C_{20}H_{18}N_2O_4$. Calculated: C 68.6; H 5.1; N 8.0%.

2,2-Dimethylindoxyl (VI) Hydrochloride. A solution of 2.9 g (0.02 mole) of cinnamoyl chloride was added dropwise at 20°C to a solution of 3.3 g (0.02 mole) of azirine [15] in 40 ml of dry benzene, after which the benzene was removed by distillation, and the residue was dissolved in acetone. The resulting precipitate was recrystallized from ethanol to give 2.1 g (53%) of a product with mp 183-184°C. IR spectrum: 1680 (C=O) and 3470 cm^{-1} (NH). ^1H NMR spectrum (d_6-DMSO), δ: 1.76 (6H, s, CH_3), 7.54 (2H, m, H_o), 7.92 (2H, m, H_m), and 8.74 ppm (1H, s, NH). ^{13}C NMR spectrum ($CDCl_3$ and d_6-DMSO), δ: 24.1 (CH_3), 62.2 (quaternary C), 128.5 ($C_{5,6}$), 128.8 ($C_{4,7}$), 133.0 (C_9), 133.4 (C_8), and 198.8 ppm (C=O). Found: C 60.4; H 6.4; N 6.8%. $C_{10}H_{11}NO \cdot HCl$. Calculated: C 60.8; H 6.1; N 7.1%.

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