THERMAL AND HYDROLYTIC DECOMPOSITION OF DERIVATIVES OF N-(1-PIPERIDINOANTHRAQUINON-2-YL)OXAZIRIDINE

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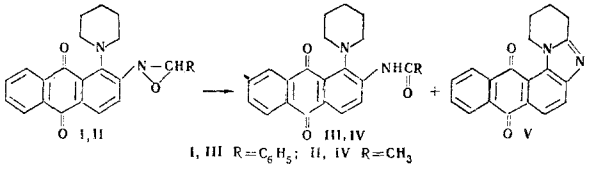
On being heated in toluene or treated with alcoholic alkalies, 3-phenyl- and 3-methyl-2-(1-piperidinoanthraquinon-2-yl)oxaziridines undergo both isomerization into 1-piperidino-2-acylaminoanthraquinones and also conversion into 8,13-dioxo-1,2,3,4,8,13-hexahydropyridyl[1,2-a]-anthra[2,1-d]imidazole.

Oxaziridines decompose comparatively readily on heating and under the action of acids, alkalis, and other reagents. The thermolysis of oxaziridines forms either nitrones or amides or products of further decomposition, depending on the conditions and the structure of the initial oxaziridines [1,2]. Schmitz and Schramm [3] observed a ring-opening reaction when N-acyl derivatives of the oxaziridines were heated in benzene or toluene.

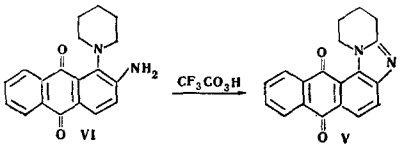
We have studied the thermal decomposition, and also the decomposition under the action of alcoholic alkalis, of 3-phenyl- and 3-methyl-2-(1-piperidine-anthraquinon-2-yl)oxaziridines (I, II), which we synthesized earlier [4]. It has been established that on being heated in toluene these compounds are converted into the corresponding 2-acylamino-1-piperidylanthraquinones (III, IV). In addition to these, in both cases we isolated from the reaction mixture a yellow crystalline compound with mp 250–252° C, $C_{19}H_{14}N_2O_2$ (V).



Oxaziridine I decomposes almost completely on prolonged (100 hours) boiling in toluene with the formation of 20% of III and 75% of compound V. On decomposition under the same conditions, oxaziridine II gave 10% of IV, 27% of V, and 58% of the initial compound. Apparently the electron-donating methyl group increases the stability of the oxaziridine ring. The lower stability of acetyl-substituted oxaziridines as compared with alkyloxaziridines has been reported previously [5].

When ethanolic solutions of oxaziridines I and II were treated with a 10% solution of NaOH or KOH, 50–60% of compound V and 35–45% of 2-amino-1-piperidylanthraquinone (VI) were obtained. The latter is formed by the hydrolysis of acylaminoanthraquinones III and IV.

On the basis of analytical and spectral results, we have come to the conclusion that V is 8,13-dioxo-1,2,3,4,8,13-hexahydropyridyl[1,2-*a*]anthra[2,1-d]-imidazole. The PMR spectrum of V has three signals of protons of methylene groups: 4.48 ppm (triplet), 3.10 ppm (triplet), and 2.00 ppm (multiplet) with a ratio of the intensities of 1 : 1 : 2. The observed spectrum is in complete harmony with the results obtained for signals of the protons of methylene groups of compounds containing an imidazole ring condensed in the 1,2-*a* position with a piperidine ring [6]. The structure of the imidazole V was confirmed by its synthesis from VI by the method of oxidative cyclization described by Nair and Adams [7].



According to the literature [8], not only ortho-substituted aromatic amines, but also their N-acetyl derivatives

are capable of cyclizing under the action of oxidizing agents with the formation of imidazole derivatives. We have studied the possibility of the formation of imidazole derivatives by boiling compounds III, IV, and VI in toluene; in this case atmospheric oxygen could be an oxidizing agent. After 100 hr of such treatment, no traces whatever of changes in the starting materials were detected by paper chromatography. Thus, only on thermolysis or alkaline hydrolysis are N-(1-piperidylanthraquinon-2-yl)oxaziridines converted into imidazole derivatives. The transformation process possibly begins with the opening of the oxaziridine ring at the N—O and N—C bonds. In both the thermal and the hydrolytic decomposition of compound I we isolated benzaldehyde from the reaction mixture in the form of the 2,4-dinitrophenylhydrazone.

EXPERIMENTAL

3-Phenyl- and 3-methyl 2-(1-piperidinoanthraquinon-2-yl)oxaziridines (I,II), 2-benzoylamino- and 2-acetylamino-1-piperidinoanthraquinones (III,IV), and 2-amino-1-piperidinoanthraquinone (VI) have been described previously [4].

The compounds obtained by thermal and hydrolytic decomposition of oxaziridines I and II were identified by comparison with authentic samples (mixed melting points, IR spectroscopy). The IR spectra were recorded on a UR-10 instrument in KBr tablets. The electronic absorption spectra were taken on a SFD-5 instrument, and the PMR spectra on a Varian A 56/60 instrument (in deuteriochloroform).

8,13-Dioxo-1,2,3,4,8,13-hexahydropyrido[1,2-*a*]anthra[2,1-d]imidazole (V). With cooling in an ice bath and stirring, 0.5 ml (17.5 mM) of 50% hydrogen peroxide was added to a solution of 200 mg (0.6 mM) of VI in 5 ml (61.7 mM) of trifluoroacetic acid, the mixture was heated in a water bath for 15 min, cooled, diluted with water, and extracted with chloroform. The extract was washed with water and with 5% sodium bicarbonate solution. Chromatography on alumina in chloroform yielded 0.13 g (60%) of V. Yellow needles, mp 250–252° C (chlorobenzene). UV spectrum (in ethanol), λ_{max}, nm (log ε): 244 (4.48), 274 (4.53), 370 (4.93). Found, %: C 75.4, 75.2; H 4.8, 4.8; N 9.6, 9.5; Molt wt (mass spectroscopy) 302. Calculated for $C_{19}H_{14}N_2O_2$, %: C 75.5; H 4.6; N 9.3. Molt wt 302.

Thermal decomposition of the oxaziridines. A) A solution of 500 mg (1.2 mm) of I in 50 ml of toluene was boiled for 100 hr. The color of the solution changed from violet-red to yellow. The mixture was cooled, treated with 200 mg (1.0 mM) of 2,4-dinitrophenyl hydrazine dissolved in 50 ml of ethanol and 2 ml of conc. HCl, left overnight, washed with water, and separated by chromatography on alumina (chloroform). This gave 100 mg (20%) of III, 280 mg (75%) of V, and 260 mg of benzaldehyde 2,4-dinitrophenylhydrazone.

B) Similarly, 500 mg of II gave 50 mg (10%) of IV, 110 mg (27%) of V, and 290 mg (58%) of the initial compound.

Alkaline hydrolysis of the oxaziridines. A) A solution of 200 mg (0.5 mM) of I in 50 ml of ethanol was treated with 0.4 ml (1.1 mM) of 10% NaOH, the mixture was boiled for 1 hr, and to the resulting solution, while it was still hot, was added 90 mg (0.45 mM) of 2,4-dinitrophenylhydrazine in 20 ml of ethanol and 2 ml of conc HCl. Then it was diluted with water and extracted with benzene. Chromatography on alumina yielded 80 mg (56%) of V, 60 mg (40%) of VI, and 70 mg of benzaldehyde 2,4-dinitrophenylhydrazone.

B) Similarly, 200 mg of II yielded 85 mg (49%) of V and 76 mg (43%) of VI.

C) With stirring, 0.5 ml (1.0 mM) of 10% KOH was added to a solution of 200 mg (0.5 mM) of I in 50 ml of methanol, and the mixture was boiled for 30 min, cooled, diluted with water, and extracted with benzene, and the extract was chromatographed on alumina. This gave 105 mg (61%) of V and 62 mg (35%) of VI.

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