PHOTOLYSIS OF AROYL AZIDES IN 2,3-DIMETHYL-2-BUTENE
2,2,3,3-TETRAMETHYL-1-AROYLAZIRIDINES AND 4,4,5,5-TETRAMETHYL-2-ARYL-2-OXAZOLINES

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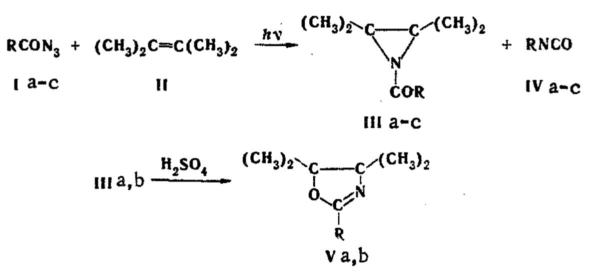
Irradiation of solutions of 2,3-dimethyl-2-butene and substituted aroyl azides in methylene chloride with UV light gave 2,2,3,3-tetramethyl-1-aroylaziridines, which are converted to 4,4,5,5-tetramethyl-2-aryl-2-oxazolines in the presence of sulfuric acid.

2,3-Dialkyl-1-benzoylaziridines are obtained when benzoyl azide and N-benzoyl-S,S-diethylsulfimide are subjected to photolysis in sym-disubstituted ethylenes [1], whereas only compounds that are isomeric with respect to the corresponding aziridines are obtained by photolysis of p-chlorobenzoyl azide (Ia) in trimethylethylene and in 1-ethoxy-2-methyl-1-propene [2].

The present research was devoted to a study of the compositions of the products formed in the photolysis of aroyl azides in 2,3-dimethyl-2-butene (II). The individual 2,2,3,3-tetramethyl-1-aroylaziridines (IIIa,b) were isolated in 10-15% yields by rapid preparative chromatography of the products of photolysis of azide Ia and 2,4-dichlorobenzoyl azide (Ib) in olefin II. We were unable to isolate 2,2,3,3-tetramethyl-1-(p-anisoyl)-aziridine, (IIIc), which was synthesized under similar conditions, in analytically pure form.



I, III-V a $R = 4\text{-}ClC_6H_4$; b $R = 2,4\text{-}Cl_2C_6H_3$; I, III, IV c $R = 4\text{-}CH_3OC_6H_4$

According to the IR and PMR spectral data and the results of thin-layer chromatography (TLC), the reaction mixtures consist of aziridines III, azides I, and aryl isocyanates IV. The PMR spectra of the reaction mixture of azide Ia in olefin II contain three A_2B_2 systems of protons, which were assigned to Ia-IIIa. The presence of aryl isocyanates IVa,c was confirmed by the presence in the IR spectra of the photolyzates (95% azide conversion) of very intense absorption at 2270 cm^{-1} (ν_{NCO}).

According to the results of quantitative analysis of the PMR spectra, the percentage of aziridine IIIa in its mixture with isocyanate IVa is almost independent of the temperature at which the azide Ia is irradiated: 43-44% at 40°C, 45-46% at 0°, and 43% at -40° (40% azide conversion). This is in agreement with the data in [1], from which it follows that the aryl isocyanates are not formed from the aroylnitrenes but directly from the aroyl azide, whereas the singlet aroylnitrenes are completely (or almost completely) tied up by olefin II to give aziridine III. The yields of the aziridines (based on the decomposed azide) decrease as the degree of conversion of the azide increases: ~45% at 40% conversion and ~30% at 95% conversion of azide Ia.

Aziridines III undergo partial isomerization under preparative thin-layer chromatography (TLC) conditions to 4,4,5,5-tetramethyl-2-aryl-2-oxazoline (V) and other compounds. Whereas aziridine IIIa was the

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only product containing methyl groups in the photolysis of azide Ia in olefin II (δ 1.32 s), a complex mixture of compounds consisting, according to the PMR spectral data, of 25% aziridine IIIa (δ 1.32), 30% oxazoline Va (δ 1.26, 1.41), and 45% of other compounds containing a $C(CH_3)_2$ fragment, was obtained in an attempt to isolate it by slow preparative chromatography on silica gel. The chromatographic isolation of the aziridines from the photolyzates therefore, involves loss of the substances. Thus, according to the PMR spectral data, a total of ~30% (in the case of irradiation of azide Ia), ~50% (in the case of irradiation of azide Ib), and 36% (in the case of irradiation of azide Ic) of aziridines IIIa-c were present in the photolyzates in the case of 95% conversion of the azides. Aziridines IIIa-c were obtained in 11, 22, and 19% yields, respectively, by preparative TLC of these photolyzates.

Aziridines IIIa,b are converted to the corresponding oxazolines (Va,b) in the presence of sulfuric acid. This transformation can be accomplished without isolation of the aziridine from the photolyzate if isocyanate IV, which is present in the photolysis products, is removed by treatment of the photolyzate with aniline.

EXPERIMENTAL

The IR spectra were obtained with a UR-20 spectrometer. The UV spectra were obtained with a Perkin–Elmer 402 spectrophotometer. The PMR spectra were recorded with a Varian-HA-100 spectrometer with CH_2Cl_2 as the internal standard. The percentages of the aziridines in the reaction mixtures were determined from the ratio of 1/12 of the areas of the $C(CH_3)_2$ signals (δ 1.25-1.36) to 1/4 of the area of all of the aromatic protons or to 1/3 of the area of the CH_3O group of a methyl p-chlorobenzoate standard (δ 3.8) at a PMR spectral scanning rate of 0.5 Hz/sec. Isocyanates IVa-c were determined by the addition of a known excess of a standard solution of diisobutylamine in chlorobenzene to an aliquot of the photolyzate with subsequent back titration with 0.1 N HCl solution in the presence of bromphenol blue. The amount of decomposed azide was monitored from the volume of evolved nitrogen. The data on the percentages of I and IV in the reaction mixtures were in agreement with the data on their percentages obtained from the PMR spectra: the isocyanates were determined from the area of the signal of the protons in the ortho position relative to the NCO group (IVa, δ 6.95 d), and the azides were determined from the area of the signal of the protons in the ortho position relative to the CON_3 group (Ia, δ 7.72 d). Thin-layer chromatography was carried out on Silufol UV-254, and preparative TLC was accomplished on LS 5/40 silica gel with a luminescent indicator; the eluent in all cases was hexane–ether (1:1). The photolysis of Ia-c was carried out with a DRL-125 high-pressure mercury lamp (125 Wt, λ_{max}366 nm) in a quartz reactor of the immersible type with a double excess of the olefin and a 30-60-fold excess of dry methylene chloride, which had been previously washed to remove HCl and fractionated with a column.

2,4-Dichlorobenzoyl Azide (Ib). A solution of 0.5 mole of 2,4-dichlorobenzoyl chloride in 100 ml of acetone was added in the course of 15 min at 0° to a solution of 0.6 mole of sodium azide in 300 ml of 30% aqueous acetone; after 45 min, the mixture was poured into water, and the precipitate was removed by filtration, washed with water and methanol at −10°, and dissolved in hexane. The hexane solution was cooled to −60° to precipitate azide Ib (89%) with mp 52-53°. The dry product could be stored satisfactorily at 6°; appreciable decomposition occurred in solution above 0°. Azides Ia,c were similarly obtained at 15°; after recrystallization from ethanol, Ia was obtained in 61% yield (mp 41-42°) and Ic was obtained in 70% yield (mp 67-68°).

2,2,3,3-Tetramethyl-1-aroylaziridines (IIIa-c). A solution of 4.97 g (27.5 mmole) for azide Ia and 4.61 g (55 mmole) of olefin II in 100 ml of methylene chloride was irradiated at 5° for 2.5 h, after which the highly volatile compounds were removed by vacuum distillation without heating. Double preparative TLC of the residue yielded 0.72 g (11%) of an oil with R_f 0.56, which began to crystallize after 5 days. The product was frozen out from ether at -60° to give 0.65 g (10%) of aziridine IIIa with mp 74.5-75°. IR spectrum (CCl_4): 1667, 1305 cm^{-1}. UV spectrum, λ_{max} (log ε): 243 (4.46, hexane); 246 nm (4.53, ethanol). PMR spectrum (CCl_4): δ 1.32 s, 7.36 d, and 7.93 d (J = 8.5 Hz). Found: C 65.4; H 6.8; N 5.9%. $C_{13}H_{16}ClNO$. Calculated: C 65.7; H 6.8; N 5.9%.

Under similar conditions, photolysis of 4.68 g of azide Ib at -40° gave, after TLC, 1.06 g (22%) of an oil with R_f 0.50, which was purified twice by TLC and began to crystallize by freezing out from hexane at -60° to give 0.71 g (15%) of aziridine IIIb with mp 88-88.5°. IR spectrum (CCl_4): 1678 and 1303 cm^{-1}. UV spectrum, λ_{max}: 237 nm (log ε 4.20 in hexane and methanol). PMR spectrum (CCl_4): δ 1.36 s, 7.36, 7.53, and 7.58. Found: C 57.2; H 5.0; N 5.0%. $C_{13}H_{15}Cl_2NO$. Calculated: C 57.3; H 5.6; N 5.1%.

Photolysis of 3.60 g of azide Ic gave, after TLC, 0.89 g (19%) of crude aziridine IIIc with R_f 0.43, which could not be purified by repeated TLC on silica gel and column chromatography on an aluminum oxide. PMR spectrum (CCl_4): δ 1.25 s, 3.81 s, 6.83 d, and 7.61 d (J = 9 Hz). IR spectrum (CCl_4): 1662 and 1295 cm^{-1}.

4,4,5,5-Tetramethyl-2-aryl-2-oxazolines (Va,b). A mixture of 0.40 g (1.7 mmole) of aziridine IIIa in 10 ml of 96% sulfuric acid was heated at 100° for 15 min, after which the acid was neutralized with aqueous carbonate solution, and the oxazoline was extracted with chloroform. The extracts were dried with magnesium sulfate and vacuum evaporated. Recrystallization of the residue from hexane gave 0.32 g (82%) of oxazoline Va with mp 56.5-57°. IR spectrum (CCl_4): 1645 and 1075 cm^{-1}. UV spectrum, λ_{max} (log ε): 248 (4.52, in hexane); 250 nm (4.42, in ethanol). PMR spectrum (CCl_4): δ1.26 s, 1.41 s, 7.39 d, and 7.73 d (J = 8.5 Hz). Found: C 66.0; H 7.2; N 5.8%. $C_{13}H_{16}ClNO$. Calculated: C 65.7; H 6.8; N 5.9%.

Oxazoline Vb, with mp 83.5-84° (from hexane), was similarly obtained in 90% yield. IR spectrum (CCl_4): 1645 and 1063 cm^{-1}. UV spectrum, λ_{max} (log ε): 242 (4.54, in hexane) and 239 nm (4.52, in ethanol). PMR spectrum (CCl_4): δ 1.28 s, 1.41 s, 7.35, 7.58, and 7.83. Found: C 57.3; H 5.8; N 5.0%. $C_{13}H_{15}Cl_2NO$. Calculated: C 57.3; H 5.6; N 5.1%.

Aniline (an equimolar amount with respect to isocyanate IVa) was added to the products of photolysis of azide Ia in olefin II, and the precipitate was separated. The highly volatile compounds were removed in the vacuo from a portion of the solution containing, according to the PMR spectral data, 1.26 mmole of aziridine IIIa, and 7 ml of concentrated sulfuric acid was added dropwise with ice cooling to the residue. After 2 h, the mixture was worked up by the method described above to give, after vacuum distillation, 190 mg (64%) of oxazoline Va with mp 50-50.5° and bp 92-93° (10 mm).

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ELECTROPHILIC SUBSTITUTION OF ACETAMIDO- AND ACETOXYBENZO-1,4-DIOXANES

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The products of acylation, bromination, and nitration of 5- and 6-acetamido- and 5- and 6-acetoxybenzo-1,4-dioxanes were established. It is shown on the basis of calculations by the self-consistent field (SCF) MO LCAO method that the directions of the electrophilic substitution reactions of these derivatives and of benzo-1,4-dioxane correspond to the π-electron population of the AO of the carbon atoms of the aromatic ring stipulated by the boundary occupied MO.

Substitution of acetamido- and acetoxybenzo-1,4-dioxanes and subsequent removal of the N- or O-acetyl substituents may serve as a method for the synthesis of new amino and hydroxy derivatives of this series, which are of interest for the preparation of physiologically active substances [1]. However, this synthetic method has not yet been developed sufficiently.

We have established that the reaction of 5-acetamidobenzo-1,4-dioxane (I) with acetyl or butyryl chlorides in the presence of $AlCl_3$ in carbon disulfide gives three acyl derivatives (II-IV or V-VII), whereas reaction in nitrobenzene gives practically only isomers III or VI, which are the products of thermodynamic control. The products of kinetic control (II, IV or V, VII) are converted to isomers III or VI when they are heated with $AlCl_3$ in nitrobenzene. Addition and reverse splitting out of substituents consequently occur at higher rates in the ring 6 and 8 positions than in the 7 position.

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