REACTION OF BIS(2-OXOCYCLOHEXYL)METHANE WITH HYDROGEN SELENIDE

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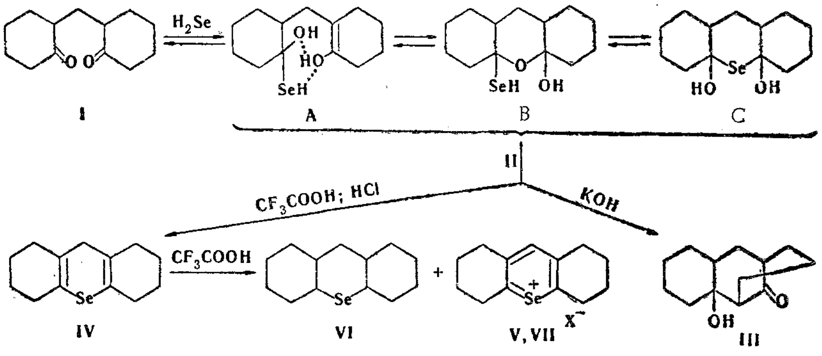
Bis(2-oxocyclohexyl)methane reacts with hydrogen selenide in polar solvents without a catalyst to give a product of nucleophilic addition of hydrogen selenide at one of the carbonyl groups, which exists in the form of three equilibrium forms, viz., 2-hemolselenolcyclohexyl-2-cyclohexanonylmethane, perhydroselenoxanthene-11,13-diol, and perhydro-11-xanthenol-13-selenol. The latter under the influence of an alcohol solution of alkali form 2,3-tetramethylenebicyclo[3.3.1]nonanon-9-ol, with hydrogen chloride; they react with hydrogen chloride to give sym-octahydroselenoxanthene, and trifluoroacetic acid converts them to a mixture of sym-octahydroselenoxanthylium trifluoroacetate and perhydroselenoxanthene. The trifluoroacetate reacts with perchloric acid to give sym-octahydroselenoxanthylium perchlorate.

Noncyclic 1,5-diketones react with hydrogen selenide and strong acids to give selenopyrylium salts [1]. We investigated the behavior of bis(2-oxocyclohexyl)methane (I) with respect to hydrogen selenide in the absence of strong acids. It is known [2] that 1,5-diketones do not react with hydrogen selenide without a catalyst.

We found that diketone I is capable of adding one molecule of hydrogen selenide to give II in polar organic solvents (CH_3COOH, CH_3OH, and CH_3NO_2). The reaction proceeds smoothly when solutions of diketone I are saturated with hydrogen selenide for 2-4 h, although we did not observe the complete conversion of I to II as a consequence of the reversibility of the reaction. Nucleophilic addition did not occur under similar conditions with hydrogen sulfide. Similar character of the conversion was observed in the reaction of diketone I with hydrogen sulfide; however, the process was carried out in the presence of morpholine [3, 4].

The successful reaction of diketone I with H_2Se in the absence of catalysts is apparently promoted by its considerably higher acidity ($K_1H_2Se = 1\cdot10^{-4}$) as compared with hydrogen sulfide ($K_1H_2S = 9\cdot10^{-8}$), which is sufficient for activation of the carbonyl group. Compound II readily eliminates hydrogen selenide in solutions (especially on contact with air oxygen) and is converted to starting diketone I. Treatment of a methanol solution of II with alkali leads to its quantitative conversion to a product of intramolecular aldol condensation of diketone I, viz., 2,3-tetramethylenebicyclo[3.3.1]nonan-9-on-2-ol (III). Catalytic amounts of hydrochloric acid give rise to the smooth conversion of II to sym-octahydroselenoxanthene (IV), whereas the action of CF_3COOH leads to sym-octa-



V $X = CF_3COO^-$; VII $X = ClO_4^-$

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hydroselenoxanthylium trifluoroacetate (V), which was identified in the form of the perchlorate (VII), and perhydroselenoxanthene (VI), which are products of disproportionation of the intermediately formed sym-octahydroselenoxanthene (IV).

The character of the chemical transformations, the results of elementary and spectral analysis, and the literature analogies [3, 4] make it possible to represent the product of nucleophilic addition of hydrogen selenide to diketone I as II, which exists in three forms, viz., A, B, and C, which undergo transformations, as a function of the reaction conditions, to the corresponding heterocyclic compounds.

The IR spectrum of hemolselenol II (A, B, C) contains a diffuse intense ν_{OH} band at 3300 cm^{-1} and a band of medium intensity at 1200 cm^{-1}, but absorption at 1500-1800 cm^{-1} is absent. The IR spectrum of IV contains C=C absorption bands at 1446 and 1675 cm^{-1}. The spectrum of perchlorate VII contains intense absorption bands of a selenopyrylium cation at 1550 and 1560 cm^{-1}. The spectrum of saturated perhydroselenoxanthene (VI) does not contain absorption bands at 1500-1800 cm^{-1}.

EXPERIMENTAL

The conversion of diketone I to II and the purity of the reaction products were monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates in a hexane—ether system (100:1) and by gas—liquid chromatography (GLC) with an LKhM-8MD chromatograph with a 2-m long stainless steel column with a diameter of 3 mm filled with 10% Apiezon-L on Chromaton N-AW-DMCS; the carrier gas was argon. The IR spectra of suspensions of the compounds in mineral oil and hexachlorobutadiene were recorded with a UR-20 spectrometer with a KBr prism.

Perhydroselenoxanthene-11,13-diol (II). A stream of nitrogen was passed with stirring in the course of 30 min through a solution of 6.24 g (30 mmole) of the threo form of diketone I (mp 55-57°C), after which H_2Se was passed through the solution at 17-18°C for 4 h. The colorless crystalline precipitate was separated, washed with cold ether, and dried *in vacuo* to give 5.6 g (65%) of II with a melting point in a sealed capillary (Ar) of 84-86°C (dec., from ether). Found: C 54.4; H 8.0%. $C_{13}H_{22}O_2Se$. Calculated: C 54.0; H 7.7%.

The reaction was carried out in CH_3OH and CH_3NO_2 at —10°C as described above, and 71 and 56% II, respectively, were obtained. No melting-point depression was observed for mixtures with the sample obtained in the preceding experiment.

Decomposition of Perhydroselenoxanthene-11,13-diol (II). A 2.89-g (10 mmole) sample of II was suspended in 50 ml of methanol, and a gentle stream of air was passed through the suspension for 48 h. The mixture was then filtered to remove the precipitated selenium, and the solvent was removed by distillation. The oily residue was recrystallized from hexane to give 1.9 g (91%) of diketone I with mp 55-57°C (58°C [5]). A mixture of the product with a genuine sample of diketone I melted without depression at 55-57°C.

2,3-Tetramethylenebicyclo[3.3.1]nonan-9-on-2-ol (III). A 2.89-g (10 mmole) sample of II was suspended in 50 ml of methanol, 1.12 g (20 mmole) of KOH was added, and the mixture was stirred for 24 h. The solvent was removed by distillation, and the residue was recrystallized from methanol to give 2 g (96%) of III with mp 168-170°C (169-171°C [5]). No melting-point depression was observed for a mixture of the product with a genuine sample of III.

sym-Octahydroselenoxanthene (IV). A 2.89-g (10 mmole) sample of II was suspended in 25 ml of CH_3COOH, 0.25 ml of concentrated HCl was added, and the mixture was stirred for 30 min. The reaction mass was then diluted with water and dried over Na_2SO_4. The solvent was then removed by distillation in a stream of nitrogen, and the pale-yellow oily residue was purified by chromatography with a column filled with Al_2O_3 (20 by 2 cm) by elution with hexane to give 2.1 g (84%) of sym-octahydroselenoxanthene (IV) in the form of a pale-yellow oil with n_D^{20} 1.5814. Found: C 62.5; H 7.2%. $C_{13}H_{18}Se$. Calculated: C 61.9; H 6.8%.

sym-Octahydroselenoxanthylium Trifluoroacetate (V) and Perchlorate (VII). A 2.89-g (10 mmole) sample of II was stirred in 9.12 g (80 mmole) of CF_3COOH for 2 h, after which 2 g (10 mmole) of 50% $HClO_4$ was added. After 15 min, the reaction mass was diluted slowly with 100 ml of ether, and the colorless crystalline precipitate of sym-octahydroselenoxanthylium perchlorate (VII) was separated, washed with ether, and dried to give 1.72 g

(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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