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OXIDATION OF PENTAFLUORO-N-(2,3,4,5,6-PENTAFLUOROBENZYLIDENE)ANILINE

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Oxidation of Schiff bases by peracids usually leads to formation of oxaziridines by means of orthogonal attack of a peracid on the C atom of the azomethine bond. In those instances when an attack in such a direction is sterically hindered an electrophilic attack of the reagent on the unshared electron pair of the N atom can take place, leading to the formation of nitrones [1, 2]. We have previously shown that anils of polyfluorobenzophenones are oxidized by CF_3CO_3H in CH_2Cl_2 at $\sim 20^{\circ}C$ yielding polyfluorosubstituted $\alpha, \alpha-N$ -triaryl nitrones. At the same time the sterically less strained anil of pentafluorobenzaldehyde (I) does not form a nitrone under these conditions. The main products of the reaction are the anilides of pentafluorobenzoic acids and pentafluorobenzaldehyde [3].

In the work in question we investigated the reaction of oxidation of pentafluoro-N-(2,3,4,5,6-pentafluorobenzylidene)aniline (II) and showed that it proceeds readily on reaction with ArOOH* at $\sim 20^{\circ}$ C, with formation of compound (III) which liberates iodine from an acidified aqueous solution of KI. NH and OH stretching absorption bands are observed in its IR spectrum (at 3410 and 3540 cm⁻¹). The PMR spectrum of compound (III) taken in CCl₄ contains signals at 5.00, 6.44 and 7.74 ppm in which the first two signals form an AB system with J = 12 Hz. The right hand component of the AB system is wide and in all probability pertains to the H atom of the NH group; the wide signal at 7.74 ppm can be attributed to the OH group [4]. As might be expected, addition of deuteromethanol to the solution of compound (III) in CCl₄ causes the disappearance of the signals of the NH and OH groups and at the same time the signal corresponding to the CH group becomes a singlet. These data as well as the nature of the ¹⁹F NMR spectrum containing signals of two different pentafluorophenyl groups make it possible to identify the compound (III) thus obtained as α -pentafluoroanilino-2,3,4,5,6-pentafluorobenzylhydroperoxide.



It can be assumed that the first step in the oxidation of compound (II) is acid-catalyzed addition of a molecule of the peroxide to the C=N bond. The second step of the reaction (intramolecular nucleophilic substitution) usually leads to the formation of oxaziridines [1] appearing hindered in the case of compound (II) as a result of the ionigenic nucleophilicity of the N atom linked with the C_6F_5 acceptor group. The formation of the hydro-

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Fig. 1. PMR spectra; 1) α -pentafluoroanilino-2,3,4,5,6pentafluorobenzylhydroperoxide in CCl₄; 2) α -pentafluoroaniline-2,3,4,5,6-benzylhydroperoxide in CCl₄ with addition of CD₃OD; 3) bis(α -pentafluoroanilino-2,3,4,5,6-pentafluorobenzyl)peroxide in (CD₃)₂CO.

peroxide (III) and not the perester of acetic acid may be caused by the instability of the latter under the reaction conditions.

Because the AcOOH solution always contained traces of H_2O_2 [5] one can not exclude the possibility of formation of hydroperoxide (III) by addition of a molecule of H_2O_2 to the azomethine bond of the original Schiff base. In the literature are described [6] the formation of the α -aminohydroperoxides of type (III) from imines of aliphatic aldehydes and ketones by reaction with H_2O_2 . In accordance with this the oxidation of compound (II) by 90% H_2O_2 also leads to hydroperoxide (III).*

It has been shown that α -aminohydroperoxides readily form oxaziridines on heating in benzene or toluene [6, 7]. Hydroperoxide (III) is also an unstable compound and on heating for a short time (1 h) at 100°C until molten and also on refluxing in alcohol goes over completely and in benzene partially to compound (V). In the IR spectrum of the latter is observed a wide absorption band of medium intensity in the NH stretching region (3420 cm⁻¹). The PMR spectrum of compound (V) contains signals corresponding to an AB system with J = 12 Hz (see Fig. 1). In the ¹³C NMR spectrum the atom of C joined to the H atom gives a signal at 85.14 ppm, i.e., it is found in an sp³ hybridized state; the results of elemental analysis and the molecular weight values determined by a vapor phase osmometry method correspond to the molecular formula C₂₆H₄F₂₀N₂O₂. All of these data allow us to assign compound (V) the structure bis(α -pentafluoroanilino-2,3,4,5,6-pentafluorobenzyl)peroxide. In accordance with this, compound (V) liberates iodine from an acidified solution of KI

$$(\text{III}) \xrightarrow{\Delta \text{ OI}} \begin{bmatrix} 2\mathbf{C}_{6}\mathbf{F}_{5}\text{CHNHC}_{6}\mathbf{F}_{5} \\ \vdots \\ 0 \end{bmatrix} \xrightarrow{} (\mathbf{C}_{6}\mathbf{F}_{5}\text{CHNHC}_{6}\mathbf{F}_{5})_{2}\mathbf{O}_{2} \\ (\mathbf{V}) \\ (\mathbf{V}\mathbf{I}) \end{bmatrix}$$

Because alkyl hydroperoxides can undergo thermal and photolytic homolysis at the 0-0 bond [8, 9] we presume that the reaction of transformation of hydroperoxide (III) into compound (V) includes intermediate formation and subsequent recombination of the oxybenzyl radicals (VI). In agreement with this, photolysis of compound (III) in the solid state in benzene leads to its rapid transformation to peroxide (V).

*By reaction of compound (I) with AcOOH or 90% H₂O₂ in CH₂Cl₂ its partial transformation was observed with formation of a mixture of compounds containing active oxygen and readily converted in solution to the original anil.

EXPERIMENTAL

UV spectra were taken on a Specord UV-VIS spectrophotometer in ethanol. IR spectra on the UR-20 apparatus. ¹³C NMR spectra were recorded on the Bruker WP-22-SY apparatus in deuteroacetone, the PMR and ¹⁹F NMR were taken on the Varian A56/60 A apparatus. HMDS in C_6F_6 was used as the internal standard. The ¹⁹F chemical shifts were determined in ppm from CCl_3F , in which $\Delta\delta$ for C_6F_6 and CCl_3F was taken as 163.9 ppm. The molecular weight determination was made by a vapor phase osmometry method in CHCl₃.

Pentafluoro-N-(2,3,4,5,6-pentafluorobenzylidene)aniline (II) was synthesized according to the method of [10].

Oxidation of Benzylideneaniline (II). a) To a solution of 0.72 g of (II) in 10 ml CH_2Cl_2 was added dropwise a solution of AcOOH prepared from 0.96 ml of Ac_2O or 0.56 ml of AcOH and 0.28 ml of 90% H_2O_2 in 10 ml CH_2Cl_2 and the reaction mixture stirred 6 h at $\sim 20^{\circ}C$ in a flask covered with dark paper. The mixture was poured into ice, extracted with ether, the ether solution washed with aqueous NaHCO₃, water, dried over anhydrous MgSO₄, the solvent distilled off and the residue washed with 40-70°C bp petroleum ether. Obtained 0.66 g (85%) of α -pentafluoroanilino-2,3,4,5,6-pentafluorobenzylhydroperoxide (III), mp 68-70°C (from 40-70°C bp pet. ether). UV spectrum ($\overline{\lambda}_{max}$, nm, log ε): 224 (4.26), 258 sh (3.62). IR spectrum (CCl₄, ν , cm⁻¹): 3410 (NH), 3540 (OH). PMR spectrum (CCl₄, δ , ppm): 5.00 and 6.44 (NH-CH, AB system, J = 12 Hz), 7.74 (OH), ¹⁹F NMR (THF, δ , ppm): 142.7; 154.7; 156.2; 163.1; 165.3; 168.6 (2:1:2:2:2:1). Found: C 39.98; H 0.84; F 47.46; N 3.50. C₁₃H₃F₁₀O₂. Calculated: C 39.51; H 0.76; F 49.01; N 3.54%.

b) A solution of 0.36 g of (II) and 0.1 ml of 90% H_2O_2 was let stand 24 h at $\sim 20^{\circ}C$ then the reaction mixture was poured into water, extracted with ether. The ether solution was washed with water, dried over anhydrous MgSO₄, the solvent evaporated. A mixture (0.37 g) was obtained from its ¹⁹F NMR spectral data and contained hydroperoxide (III) and the starting compound (II) in a 3:1 ratio.

Thermolysis of Hydroperoxide (III). a) Compound (III) (0.2 g) was heated 1 h at 100°C (in a bath). The reaction mixture was cooled and washed with alcohol. There was obtained 0.17 g (90%) of bis(α -pentafluoroanilino-2,3,4,5,6-pentafluorobenzyl)peroxide (V), mp 126-128°C (from 70-1-0°C bp pet.ether). UV spectrum (λ_{max} , nm, log ε) 256 (4.53), 323 sh (3.98). IR spectrum (CHCl₃, ν , cm⁻¹): 3420 (NH), PMR spectrum ((CD₃)₂CO, δ , ppm): 5.90 and 6.64 (NH-CH, AB system, J = 12 Hz).¹⁹F NMR spectrum (THF, δ , ppm): (2:1:2:2:2:1). Found: C 41.76; H 0.84; F 49.85; N 3.70%, molecular weight 714. C₂₆H₄F₂₀N₂O₂. Calculated: C 41.29; H 0.53; F 50.25; N 3.70%; molecular weight 756.

b) A solution of 0.2 g of (II) in 5 ml alcohol was refluxed 1 h. The solvent was distilled off. The product isolated (0.16 g) was identified as compound (V) by its melting point and its ¹⁹F NMR spectrum.

<u>UV Radiation of Hydroperoxide (III)</u>. a) A solution of 0.2 g of (III) in 10 ml of benzene was placed in a glass test tube and irradiated 1 h with a DRSh-500 mercury lamp placed at a distance of about 30 cm at \sim 20°C. The product isolated by distilling off the solvent was washed with alcohol yielding 0.17 g (90%) of peroxide (V).

b) Finely pulverized (III) (0.1 g) was placed between two flat glass plates closed by compression and irradiated 2 h with a DRSh-500 mercury lamp at a distance of \sim 40 cm. The product obtained was washed with alcohol. Yield 0.08 g (82%) of peroxide (V).

CONCLUSIONS

The reaction of pentafluoro-N-(2,3,4,5,6-pentafluorobenzylidene)aniline with peracetic acid or 90% hydrogen peroxide in CH_2Cl_2 at $\sim 20^{\circ}C$ yields α -pentafluoroanilino-2,3,4,5,6pentafluorobenzylhydroperoxide. Its capability for thermal and photolytic transformation into bis(α -pentafluoroanilino-2,3,4,5,6-pentafluorobenzyl)peroxide was shown.

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THE TRANSMISSION POWER OF A BRIDGING MERCURY ATOM

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Earlier during investigation of the transmission power of a bridging mercury atom in systems of the $ArHgC_{3}H_{4}F-4$ (I) type by the ¹⁹F NMR method it was established that the transmission of the electronic effects of substituents along the Hg-C_{ar} bonds takes place by an inductive mechanism, and the mercury atom has a lower transmission power than a bridging CH₂ group [1]. However, the quantitative result on the relative effectiveness of the transmission of the electronic effects of the substituents through a mercury bridge can only be regarded as tentative, since the previously obtained data [1] on the chemical shifts of fluorine caused by the substituent for (I) were compared with published data for structurally related compounds of the $ArCH_2C_6H_4F-4$ (II) [2] type, which were determined in solvents similar in nature but not identical. Moreover, the number of compounds in series (I) and (II) with identical Ar groups was small, which (as known) has a significant effect on the quality of the statistical treatment of the experimental results.

In order to obtain quantitative data on the relative conduction of the electronic effects on the substituents by the bridging mercury atom in the present work we synthesized a series of substituted 4-fluorodimethylmethanes with a standard set of variable aromatic radicals (IIa, c-k), where $Ar = 4-Me_2NC_6H_4$ (a), $4-MeOC_6H_4$ (b), $4-MeC_6H_4$ (c), Ph (d), $4-FC_6H_4$ (e), $3-FC_6H_4$ (f), $4-ClC_6H_4$ (g), $3-ClC_6H_4$ (h), $3-CF_3C_6H_4$ (i), $3,4-Cl_2C_6H_3$ (j), $3,4,5-Cl_3H_6H_2$ (k), and we determined the chemical shifts of fluorine (δF) in chlorobenzene (Table 1). In addition, in order to study the effect of the nature of the solvents on the transmission power of mercury we determined the δF values for series (I) and (II) in solvating (pyridine, DMSO) and nonsolvating polar (nitrobenzene, DCE) solvents (Table 1). It should be noted that in the present work, as in [1], the data on the δF values of (I) were obtained during analysis of the PMR spectra of the equilibrium mixtures formed during the reaction of 4-FC_6H_4)_2Hg with Ar_2Hg .

For a quantitative assessment of the relative transmission power of the bridging mercury atom we made a correlation of the data on the δF values in chlorobenzene for (I) in relation to the δF values for the corresponding compounds (II). The tangent of the slope of the obtained straight line (Table 2, No. 1) indicates that the mercury atom has a lower transmission power than the CH₂ group. However, the differences in the effectiveness of the transmission of the electronic effects of the substituents through the -Hg and -CH₂ bridges amounts to \sim 30% and not 50%, as we supposed earlier [1].

Whereas our previously obtained correlation data for systems (I) (Table 2, Nos. 2 and 3) clearly demonstrate the inductive character of the transmission of the electronic effects of the substituents in them, the extremely insignificant differences in the quality of the correlations between δF of (II) and the σ_p^0 or σ_p constants (Table 2, Nos. 4 and 5) indicate that other factors not realized in (I) make a substantial contribution in (II) in addition

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