CONCLUSIONS

1. The substitution of a para hydrogen atom by fluorine in monofunctional benzene derivative having C_{2v} or pseudo-C_{2v} symmetry may be useful for determining the symmetry of the HOMO.

2. The highest occupied molecular orbital in N-sulfinylaniline and N-sulfinyl-4-fluoroaniline has a_2 symmetry, while the following orbital (HOMO-1) has b_1 symmetry. The order is reversed in N-sulfinyl-2,3,5,6-tetrafluoroaniline and N-sulfinylpentafluoroaniline.

3. The N-sulfinyl group interacts with the p-fluorophenyl ring similarly to a nitro group, i.e., as a strong electron-withdrawing substituent.

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AN INTRAMOLECULAR NUCLEOPHILIC FLUORINE SUBSTITUTION REACTION — A PATHWAY TO THE SYNTHESIS OF POLYFLUORODIBENZ[b,f]-1,4-OXAZEPINES

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UDC 542.91:547.892:66.095.252:547.551.51

The intramolecular nucleophilic substitution of the ortho-fluorine atoms in polyfluoroaromatic compounds is a convenient and common method for the synthesis of polyfluorinated five- and six-membered benzheterocycles [1, 2]. Two examples of the formation of seven-membered heterocycles by this method have also been reported [3, 4].

We have discovered that N-pentafluorobenzylidene-o-hydroxyaniline prepared from pentafluorobenzaldehyde and o-aminophenol according to Weygand-Hilgetag loses a fluoride ion upon brief heating in DMF at 100°C and forms a quantitative yield of 1,2,3,4-tetrafluorodibenz-[b,f]-1,4-oxazepine (II).* The structure of (II) was supported by elemental analysis and ^1H and ^{19}F NMR spectroscopy.

Oxazepine (II) is also formed from (I) upon prolonged maintenance in DMF at about 20°C or upon heating in ethanol at reflux.

The facility of this reaction is a consequence of the high lability of the fluorine atom in the position ortho to the azomethine substituent, the sufficient acidity of the OH group and, apparently, the proximity of the reaction sites. Hence, thin-layer chromatography and ^{19}F NMR spectroscopy indicates that, under analogous conditions, N-pentafluorobenzyl-o-hydroxyaniline (III) does not give 10,11-dihydro-1,2,3,4-tetrafluorodibenz[b,f]-1,4-oxazepine (IV).

*2-Nitro[b,f]-1,4-oxazepine has been obtained from the sodium salt of N-(2-chloro-5-nitrobenzylidene)-o-hydroxyaniline by brief heating in DMF at reflux [6].

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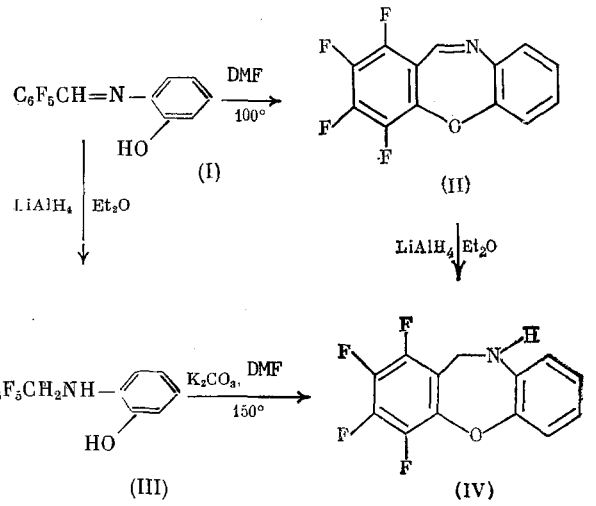
Translated from Izvestiya Akademii Nauk USSR, Seriya Khimicheskaya, No. 2, pp. 477-478, February, 1986. Original article submitted May 24, 1985.

An authentic sample of (IV) was obtained by the reduction of (II). The conversion of (III) to (IV) is observed only under more vigorous conditions in the presence of K_2CO_3.



This reaction permits the synthesis of polyfluorodibenz[b,f]-1,4-oxazepines whose non-fluorinated analogs have found use as antidepressants [7]. We are studying the possibility of the similar conversion of polyfluoroaromatic azomethine with other functional groups.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer. The ^1H and ^{19}F NMR spectra were taken on a Varian A56/60A spectrometer at 60 and 56.4 MHz. The ^{19}F NMR chemical shifts were measured relative to C_6F_6. The molecular weight was determined on an MS-3301 high-resolution mass spectrometer.

N-Pentafluorobenzylidene-o-hydroxyaniline (I). Equimolar amounts of pentafluorobenzaldehyde and o-aminophenol were mixed. Warming of the reaction mass was noted. The mixture was maintained for 0.5 h and treated with ethanol. Fluoride ions were not lost. The residue was filtered off and washed with ethanol and hexane to give 90% (I), mp 185-186°C (dec., from ethanol). IR spectrum (KBr, ν, cm^{-1}): 3380 (OH). Found, %: C 54.31; H 2.11; F 32.83; N 4.97%; mol. wt., 287. $C_{13}H_6F_5NO$. Calculated, %: C 54.37; H 2.11; F 33.08; N 4.88, mol. wt., 287.

1,2,3,4-Tetrafluorodibenz[b,f]-1,4-oxazepine (II). A sample of 0.29 g (1 mmole) (I) in 10 ml dry DMF was heated for 15 min at 100°C. The reaction mixture was poured into water and the residue was filtered off. Titration of the filtrate by zirconium oxychloride indicated 1 mg-at fluorine. A yield of 0.27 g (99%) (II) was obtained, mp 126-127°C (from ethanol). PMR spectrum ($(CD_3)_2CO$, δ, ppm): 7.28 br. s. (Ar), 8.64 s (=CH). ^{19}F NMR spectrum (THF, δ, ppm): 1.1, 5.8, 12.4, 18.6 (1:1:1:1). Found, %: C 58.66; H 1.91; F 28.45; N 5.24 mol. wt., 267. $C_{13}H_4F_4NO$. Calculated, %: C 58.44; H 1.89; F 28.45; N 5.24 mol. wt., 267.

N-Pentafluorobenzyl-o-hydroxyaniline (III). A sample of 0.58 g (I) was added gradually to 0.16 g $LiAlH_4$ in 20 ml abs. ether at ~20°C, stirred for 0.5 h, poured onto a mixture of ice and dilute hydrochloric acid and extracted with ether. The ethereal solution was washed with aqueous $NaHCO_3$ and water, dried over $MGSO_4$, and evaporated. The residue was washed with hexane to give 0.42 g (72%) (III), mp 120-122°C (from petroleum ether, bp 70-100°C). IR spectrum (CCl_4, ν, cm^{-1}): 3440 (NH), 3610 (OH). PMR spectrum (CCl_4, δ, ppm): 4.39 s (CH_2), 4.54 br. s (NH, OH), 6.59 m (Ar). ^{19}F NMR spectrum (THF, δ, ppm): −0.4, 6.0, 21.3 (2:1:2). Found, %: C 54.14; H 2.82; F 32.80; N 4.73; mol. wt. 289. $C_{13}H_8F_5NO$. Calculated, %: C 53.99; H 2.79; F 32.85; N 4.84; mol. wt., 289.

10,11-Dihydro-1,2,3,4-tetrafluorodibenz[b,f]-1,4-oxazepine (IV). a) A sample of 0.27 g (II) was added to 0.04 g $LiAlH_4$ in 20 ml abs. ether at ~20°C, stirred for 1 h and treated as described above to give 0.23 g (85%) (IV), mp 67-68°C (sublimes at 90°C (2 mm)). IR spectrum (CCl_4, ν, cm^{-1}): 3340 (NH). PMR spectrum (CCl_4, δ, ppm): 3.70 s (NH), 4.44 s (CH_2), 6.70 m (ABCD system, Ar). ^{19}F NMR spectrum (THF, δ, ppm): −0.5, 4.4, 5.3, 15.8 (1:1:1:1). Found, %: C 58.36; H 2.50; F 28.21; N 5.11; mol. wt., 269. $C_{13}H_7F_4NO$. Calculated, %: C 58.00; H 2.62; F 28.23; N 5.20%; mol. wt., 269.

b) A mixture of 0.2 g (III) and 0.2 g dry K_2CO_3 in 9 ml dry DMF was heated for 2 h at 150°C. Then the mixture was poured in dilute hydrochloric acid and extracted with ether. The ethereal layer was washed with water, dried over $MgSO_4$, and evaporated to give 0.18 g (IV) identified by ^{19}F NMR spectroscopy.

CONCLUSIONS

N-Pentafluorobenzylidene-o-hydroxyaniline upon heating in organic solvents such as DMF and ethanol cyclizes to give 1,2,3,4-tetrafluorodibenz[b,f]-1,4-oxazepine through intramolecular nucleophilic substitution of the para fluorine atom.

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KINETICS OF THE GEMINAL RECOMBINATION OF TRIPLET RADICAL PAIRS IN GLYCERIN

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UDC 541.127:541.515:547.426.1

In our previous work [1, 2], we studied the kinetics of the geminal recombination of radical pairs (RP) in viscous solvents and magnetic effects in these reactions. In homogeneous solutions of sufficiently high viscosity ($\eta \simeq 19^2$-10^4 cP), radical pairs formed by the action of a light pulse have a rather high lifetime ($\tau_{RP} \simeq 10^{-7}$-10^{-6} sec), which permits recording of the kinetics of the annihilation of the RP. The study of the kinetics of geminal recombination which is a new region of liquid-phase kinetics has become possible only in the past decade.

In the present work, we studied the kinetics of the geminal recombination of aromatic radicals obtained upon the laser photolysis of benzophenone (BP) and 1,4-benzoquinone (BQ) at from 213 to 303°K in glycerin.

EXPERIMENTAL

A laser photolysis apparatus with photoelectric recording was used. Excitation was achieved using a PRA LN 100 nitrogen laser manufactured in Canada; the resolution time of the system was 10 nsec. In order to reduce the error in the kinetic measurements, the signal was averaged over 128-1024 flashes. The rapid processes were recorded with a Biomation 6500 unit manufactured in the United States and a Kowasaki B50 E unit with a TMS-600 averager manufactured in Japan. The cell with 1 × 1 cm cross section holding the solution studied was maintained at constant temperature. In the experiments on the effect of an external magnetic field, the cell was placed in a permanent magnet creating a field H = 0.34 T.

Samples of BQ and BP (the common designation for these two compounds is Q) were purified by standard methods. Chemically pure grade glycerin was used. Concentrated solutions of Q

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 479-481, February, 1986. Original article submitted June 6, 1985.