ACTIVATED ADDITION OF SULFUR CHLORIDES AND

SULFENYL CHLORIDES TO HEXAFLUORODIMETHYLKETENE*

S. N. Shkurak, V. V. Ezhov, A. F. Kolomiets, and A. V. Fokin UDC 542.955:546.224'13:547.446.8

The information on the electrophilic addition of sulfur chlorides to polyfluoroalkenes [2-5] indicates that the conditions and feasibility of carrying out these reactions is a function not so much of the energy characteristics of the frontier orbitals (FO) of the polyfluoroalkenes as of their symmetry [6]. This behavior is also seen in the analogous reactions of nonfluorinated ethylene compounds [7, 8], which, apparently, reflects a common feature for electrophilic addition at double bonds which proceed through $2\pi - 3d_{z^2}$ and $2\pi - 3d_{xz}$ three-center transition states.

Of the many nonfluorinated unsaturated compounds, only ketenes may be considered to be an exception to the general rule for reactivity relative to sulfur chlorides. Despite the obvious asymmetry of the π -orbital which should lead to a high-energy three-center reaction transition state, ketenes react vigorously with electrophiles at reduced temperatures [9-11]. This may be attributed to a different mechanism, i.e., the reaction proceeds through a fourcenter transition state, which is facilitated by the high electrophilicity of the cumulene group and the asymmetry of its FO.

*Previous communication, see [1].



Fig. 1. Charge distribution in ketene (I), dimethylketene (II), and hexafluorodimethylketene (III). Newman projections for (II) and (III).

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1371-1378, June, 1984. Original article submitted March 18, 1983.



Fig. 2. Localization of the HOMO (a) and LUMO (b) in ketene (I), dimethylketene (II), and hexafluorodimethyl-ketene (III).



In light of these concepts, the lack of reactivity of a highly electrophilic cumulene such as hexafluorodimethylketene toward sulfur chlorides in nonpolar media is not readily understood [1, 6]. In the present communication, we examined the factors accounting for this phenomenon.

We initially carried out quantum-chemical calculations for ketene (I), dimethylketene (II), and hexafluorodimethylketene (III) using the LCAO MO SCF method in the MNDO approximation [12, 13]. This method is one of the most developed semiempirical approaches and gives results similar to ab initio methods. The MNDO method gives satisfactory reproduction of heats of formation, molecular geometry, dipole moments, and ionization potentials of compounds, including fluorine-containing and perfluoro compounds [13].

The results of calculations carried out with full optimization of molecular geometry are given in the form of molecular diagrams in Figs. 1 and 2 and in Tables 1 and 2.

The indices obtained for the cumulenes examined confirm the obvious asymmetry of their HOMO which is localized mainly within the C=C=0 group. The LUMO of all the ketenes studied is localized predominantly in the C=0 group and has higher symmetry relative to the major plane than the HOMO. The energies of the HOMO and LUMO decreases and the difference in their energies increases with increasing electron-withdrawing properties of the substituent.

The contributions of the substituent atomic orbitals to the molecular orbitals of the C=C=O fragment provide extremely interesting information. A significant contribution of the hydrogen atoms in the ketene molecule may be noted only to the p_X orbital of the C=C bond, leading to shortening of this bond. Occupancy of the C=C bond p_Z orbital by the methyl groups is found for dimethylketene. On the other hand, the trifluoromethyl groups of hexafluorodimethylketene reduce the electron density in the p_Z orbital and increase the electron density in the p_Z orbital of the cumulene group.

Thus, hexafluorodimethylketene, in contrast to its nonfluorinated analogs, has a significantly lower HOMO and enhanced asymmetry of this MO. Furthermore, the contributions of the CF₃ groups to the p_y orbital gives a more pronounced type of π -overlap and, thus, enhanced rigidity, i.e., reduced polarizability of the cumulene group.

These structural features logically account for the sharply reduced reactivity of hexafluorodimethylketene relative to sulfur chlorides. Reactions of the reagents by a fourcenter dipolar mechanism proved possible in this case either by activation of the S—Cl bond of the sulfur chlorides or by reduction in the rigidity of the cumulene group due to specific solvation effects.

SO₂, POCl₃, benzonitrile, and acetonitrile were used as activators. Sulfur dioxide was selected as a solvent which specifically solvates only sulfur chlorides. POCl₃ and carboxylic acid nitriles, which are weak n-donors, were considered to solvate both reagents. In

| TABI | Ε1. | Energy | Ch | ara | cteri | lstics |
|------|--------|--------|----|-----|-------|--------|
| and | Dipole | Moment | s | of | (I), | (II), |
| and | (III) | | | | | |

| Com- pound | Characteristic | Value |
|----------------------|-----------------------------------------------------------------------------------|---------------------------------------------------------|
| (I) (II) (III) | Energy of the highest occupied MO, E _{HOMO} eV | $-9,290 \\ -9,091 \\ -11,612$ |
| (I) (II) (III) | Energy of the lowest unoccupied MO, E _{LUMO} eV | $\begin{array}{c} 0,337 \\ 0,279 \\ -1,775 \end{array}$ |
| (I) (II) (III) | Difference in frontier orbital energies, $\Delta E = E_{LUMO} - E_{HOMO}$, eV | 9,627 9,370 9,837 |
| (I) (II) (III) | Enthalpy of formation, kcal/mole | -7,015 -26,953 -306,835 |
| (I) (II) (III) | Dipole moment, D | 1,033 0,715 3,482 |

addition, ethers were also included in the series of solvents studied. The solvents have relatively high n-donor properties and specifically solvate electrophilic unsaturated compounds, but do not have a marked effect on the state of the S-Cl bond.

Acetonitrile was found to be the most effective activator for this reaction. In the presence of this nitrile, hexafluorodimethylketene vigorously reacts with sulfur monochloride and sulfur dichloride even below 0°C. The reaction products in the case of an equimolar reagent ratio were α -chlorocarbonylhexafluoroisopropylsulfenyl chloride (I) and α -chlorocarbonylhexafluoroisopropylsulfenyl chloride (I) and α -chlorocarbonylhexafluoroide (II), i.e., the addition proceeds in accord with the localization of the ketene FO



In acetonitrile solution, thiosulfenyl chloride (II) also adds to hexafluorodimethylketene. Bis-(α -chlorocarbonylhexafluoroisopropyl) disulfide (III) is formed almost quantitatively as a result of a slow reaction over 50-60 h at 20°C.



Sulfenyl chloride (I) does not undergo an analogous reaction, but rather displays chlorinating action



Benzonitrile less efficiently promotes these reactions than acetonitrile. In the presence of benzonitrile, sulfenyl chloride (I) and thiosulfenyl chloride (II) are formed only at 20°C; this reaction requires 15-20 h. The reaction of thiosulfenyl chloride (II) with hexafluorodimethylketene in this solvent at 20°C is complete only after 6-7 days.

The promotion effects of $POCl_3$ were found to be similar to those of benzonitrile. The first step of these reactions in this solvent is complete in 24 h at 20°C. However, the addition of hexafluorodimethylketene to sulfenyl chloride (I) and even thiosulfenyl chloride (II) in the presence of $POCl_3$ does not occur at 20°C. SO₂ proved to be a much less effective activator. The reactions of sulfur monochloride and sulfur dichloride with hexafluorodi-

| Compound | Bond | Bond length, Å | Compound | Bond angle | ω, deg |
|-------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|
| (I) (II) (III) (III) (III) (III) (III) (III) (III) (III) | $O^{1}-C^{2}$ $C^{2}-C^{3}$ $C^{3}-H^{4}$ $C^{3}-C^{4}$ $C^{3}-H^{5}$ $C^{3}-C^{5}$ | $\begin{array}{c} 1,184\\ 1,181\\ 1,167\\ 1,319\\ 1,330\\ 1,346\\ 1,084\\ 1,503\\ 1,551\\ 1,084\\ 1,503\\ 1,503\\ 1,503\\ 1,503\end{array}$ | (I), (II), (III) (I) (II) (III) (III) (III) (III) (III) (III) (III) (III) (III) (III) (III) | $\begin{array}{c} OC^2C^3\\ C^2C^3H^4, C^2C^3H^5\\ C^2CC^4; C^2C^3C^4\\ C^2C^3C^4\\ C^2C^3C^5\\ C^3C^4H^6, C^3C^5H^9\\ C^3C^5F^9\\ C^3C^5F^9\\ C^3C^5H^{11}\\ C^3C^5F^{11}\\ H^{10}C^5H^{11}\\ H^{10}C^5F^{11}\\ C^3C^4F^8\end{array}$ | 180 121,8 120,5 120,5 120,1 112,3 112,0 112,1 111,0 110,9 112,3 110,0 113,1 112,2 |
| (II) (III) | $\begin{array}{c} \mathrm{C-H}\\ \mathrm{C-F} \end{array}$ | 1,110-1,111 1,353-1,361 | | | I |

TABLE 2. Geometrical Parameters of (I), (II), and (III)

methylketene at 20° C in SO₂ are complete after 2-3 days and only sulfenyl chloride (I) and thiosulfenyl chloride (II) are formed even in a large excess of ketene.

The reaction times and addition product yields depend significantly on the solvent purity. In the presence of water, HCl, and other acid substances, the yield of the desired products is reduced and, in some cases, the reaction is entirely suppressed.

In contrast to acid nitriles, $POCl_3$, and SO_2 , diethyl ether and dimethoxyethane do not activate the addition of sulfur chloride to hexafluorodimethylketene. The additional introduction of pyridine or triethylamine to the reaction medium leads to a complex product mixture consisting of ketene dimers, chlorination products, and products of solvent chlorination. These reactions differ in this way from the previously described reaction of hexafluorodimethylketene with phenylsulfenyl chloride, which leads to the formation of the addition product in dimethoxyethane in the case of pyridine catalysis [14].

The structures of (I)-(III) were determined by spectral methods and conversions. Sulfenyl chloride (I) and thiosulfenyl chloride (II) are highly reactive and, at 20-30°C, add by a single pathway to cyclopentene to form sulfide (IV) and unsymmetrical disulfide (V)



At 130°C, sulfenyl chloride (I) rather smoothly adds to trifluoromethylethylene. However, the reaction of (I) with chlorotrifluoroethylene proceeds only at 150-160°C and leads to asymmetrical sulfide (VII), disulfide (III), and trichlorotrifluoroethane.



Disulfide (III) does not react with chloride at 20° C and is converted quantitatively to sulfenyl chloride (I) only at $90-100^{\circ}$ C.



Sulfide (III) reacts vigorously with methanol in CCl₄ and is converted to bis-(α-carbomethoxyhexafluoroisopropyl) disulfide (VIII). The same compound was obtained by convergent synthesis by the reaction of methyl 2-hydrohexafluoroisobutyrate with sulfur monochloride or sulfur dichloride in the presence of triethylamine



Phenylsulfenyl chloride, 2-trifluoromethyl-2-chloroethylsulfenyl chloride, and 2,2dichlorotrifluoroethylsulfenyl chloride were taken for a study of the conditions for the activated addition of sulfenyl chlorides to hexafluorodimethylketene. Sulfides (VI) and (IX) were obtained quantitatively in solutions of acetonitrile and SO_2 with the former two sulfenyl chlorides



2,2-Dichlorotrifluoroethylsulfenyl chloride does not form products of addition to hexafluorodimethylketene in these solvents.

Hence, the activation of the addition of sulfur chlorides and sulfenyl chlorides to hexafluorodimethylketene is accomplished only by solvents capable of specific solvation of the S-Cl bond of sulfur chlorides and sulfenyl chlorides. These solvents form the following series relative to decreasing activation capacity in the reaction studied: MeCN > PhCN > $POCl_3 > SO_2$. This series corresponds to the fall-off in their n-donor properties [15]. Hence, especially effective addition of sulfur chlorides or sulfenyl chlorides to hexafluorodimethylketene occurs upon activation of both the S-Cl bond and the cumulene group of the reagents. This hypothesis is in complete accord with the concept that these reactions proceed through a four-center dipolar transition state.

EXPERIMENTAL

Freshly distilled samples of sulfur chlorides and sulfenyl chlorides were used in the experiments. The solvents were thorougly purified and dried. The NMR spectra were taken in 1:1 CHCl₃ solutions. The chemical shifts are given on the δ scale relative to CF₃CO₂H (external standard) for ¹⁹F nuclei and relative to TMS (internal standard) for ¹H nuclei.

<u> α -Chlorocarbonylhexafluoroisopropylsulfenyl Chloride (I)</u>. a) A sample of 10.3 g SCl₂ was added to 20 ml acetonitrile and 20.0 g hexafluorodimethylketene was bubbled into the solution with mixing and maintenance of the temperature not higher than -10° C. The mixture was maintained for 4 h at from -10° to 0°C, then slowly warmed to 20°C and fractionated to yield 25.3 g (90%) sulfenyl chloride (I), bp 114-115°C, np²⁰ 1.3990. ¹⁹F NMR spectrum: -15.27 s (CF₃). IR spectrum (ν , cm⁻¹): 1745 (C=0). Found: C 16.98; F 40.30; Cl 25.31; S 11.30%. Calculated for C₄F₆Cl₂OS: C 17.10; F 40.57; Cl 25.23; S 11.41%.

In an analogous experiment using benzonitrile, 23.6 g (84%) sulfenyl chloride (I) was obtained at 20°C over 24 h.

b) A mixture of 10.3 g SCl₂, 20 ml SO₂, and 20 g hexafluorodimethylketene was maintained for two days at 20°C in a sealed ampul, shaken occasionally, cooled and fractionated to yield 21.1 g (75%) sulfenyl chloride (I), bp 114-115°C, n_D^{20} 1.3991.

Sulfenyl chloride (I) was obtained in 93% yield when the reaction was carried out in POCl₃ at 20° C for 24 h.

c) A sample of 24.55 g bis-(α -chlorocarbonylhexafluoroisopropyl) disulfide and 3.55 g chlorine was placed in a steel test tube, which was then hermetically sealed, heated at 100°C for 3 h, and cooled The contents were fractionated to yield 23.94 g (85%) sulfenyl chloride (I), bp 114-115°C, np^{2°} 1.3922. ^{1°}F NMR spectrum: -15.27 s (CF₃). IR spectrum: 1745 cm⁻¹ (C=0).

<u> α -Chlorocarbonylhexafluoroisopropylthiosulfenyl Chloride (II).</u> A sample of 13.5 g S₂Cl₂, 15 ml acetonitrile, and 17.8 g hexafluorodimethylketene was placed in a glass ampul. The ampul was sealed and maintained for 48 h. The contents were fractionated to yield 28.2 g (90%) thiosulfenyl chloride (II), bp 27°C (1 mm), n_D^{2°} 1.4440. ¹⁹F NMR spectrum: -15.90 s (CF₃). IR spectrum: 1750 cm⁻¹ (C=0). Found: C 15.10; F 36.01; Cl 22.25; S 20.43%. Calculated for C₄F₆Cl₂OS₂: C 15.35; F 36.41; Cl 22.65; S 20.48%.

Bis-(α -chlorocarbonylhexafluoroisopropyl) Disulfide (III). A sample of 13.5 g S₂Cl₂, 20 ml acetonitrile, and 35.6 g hexafluorodimethylketene was placed in a glass ampul. The ampul was sealed and maintained for 48 h. The reaction mass was fractionated to yield 41.7 g (85%) disulfide (III), bp 50°C (1 mm), n_D^{2°} 1.4110. ¹⁹F NMR spectrum: -15.30 s (CF₃). IR spectrum: 1750 cm⁻¹ (C=O). Found: C 19.50; F 46.48; Cl 14.40; S 13.00%. Calculated for C₈F₁₂Cl₂O₂S₂: C 19.57; F 46.43; Cl 14.44; S 13.06%.

<u>Reaction of Sulfenyl Chloride (I) with Hexafluorodimethylketene.</u> A mixture of 14.1 g sulfenyl chloride (I), 9.0 g hexafluorodimethylketene and 15 ml SO₂ was maintained for 30 days at 20°C in a sealed ampul and then fractionated to yield 21.5 g (84%) disulfide (III), bp 55-56°C (2.5 mm), $n_D^{2^\circ}$ 1.4112 and 12.0 g (97%) α -chlorohexafluoroisobutyryl chloride, bp 68-69°C, $n_D^{2^\circ}$ 1.3347.

<u>2-Chlorocyclopentyl 1-Chlorocarbonylhexafluoroisopropyl Sulfide (IV).</u> A sample of 3.41 g cyclopentene was added to 14.05 g sulfenyl chloride (I) with stirring and cooling. The mixture was maintained for 6 h at 30°C and then fractionated to yield 13.62 g (78%) sulfide (IV), bp 110°C (15 mm), $n_D^{2^{\circ}}$ 1.4420. ¹⁹F NMR spectrum: -15.40 s (CF₃). IR spectrum: 1750 cm⁻¹ (C=O). Found: C 30.55; H 2.08; F 32.50; Cl 20.01; S 8.93%. Calculated for C₉H₈F₆-Cl₂OS: C 30.96; H 2.31; F 32.65; Cl 20.31; S 9.18%.

<u>2-Chlorocyclopentyl l-Chlorocarbonylhexafluoroisopropyl Disulfide (V)</u>. A mixture of 15.65 g thiosulfenyl chloride (II) and 3.41 cyclopentene was heated at 40-50°C for 6 h and then fractionated to yield 15.25 g (80%) disulfide (V), bp 80°C (1 mm), $n_D^{2^\circ}$ 1.4615. ¹⁹F NMR spectrum: -15.39 s (CF₃). IR spectrum: 1750 cm⁻¹ (C=0). Found: C 28.20; H 1.95; F 29.52; Cl 18.32; S 16.35%. Calculated for C₉H₈F₆Cl₂OS₂: C 28.36; H 2.12; F 29.91; Cl 18.60; S 16.82%.

2-Trifluoromethyl-2-chloroethyl 1-Chlorocarbonylhexafluoroisopropyl Sulfide (VI). a) A mixture of 14.05 g sulfenyl chloride (I) and 7.5 g trifluoromethylethylene was heated in a steel test tube for 10 h at 120-130°C and then cooled. The contents were fractionated to yield 13.3 g (70%) sulfide (VI), bp 37°C (2 mm), $n_D^{2^\circ}$ 1.3938. ¹⁹F NMR spectrum: -15.50 m (6F, 2CF₃), -9.97 m (3F, CF₃). PMR spectrum: 3.5-4.07 m (CH, CH₂). IR spectrum: 1770 cm⁻¹ (C=0). Found: C 22.25; H 0.78; F 45.10; Cl 18.53; S 8.37%. Calculated for C₇H₃F₉-Cl₂OS: C 22.30; H 0.80; F 45.35; Cl 18.80; S 8.50%.

b) A solution of 19.9 g 2-trifluoromethyl-2-chloroethylsulfenyl chloride and 17.8 g hexafluorodimethylketene in 20 ml anh. acetonitrile was maintained at 20°C for two days and then fractionated to yield 34.6 g (92%) sulfide (VI), bp 37°C (2 mm), $n_D^{2^\circ}$ 1.3940. IR spectrum: 1770 cm⁻¹ (C=0).

2,2-Dichlorotrifluoroethyl 1-Chlorocarbonylhexafluoroisopropyl Sulfide (VII). A mixture of 14.05 g sulfenyl chloride (I) and 7.5 g chlorotrifluoroethylene was heated in a steel test tube for 10 h at 150-160°C and then cooled. The reaction mass was fractionated to yield 4.18 g (21%) sulfide (VII), bp 90°C (30 mm), $n_D^{2°}$ 1.4030. ¹⁹F NMR spectrum: --14.83 m (6F, 2CF₃), -7.92 (1F, CFC1), 0.99 m (2F, CF₂). IR spectrum: 1760 cm⁻¹ (C=0). Found: C 17.95; F 42.59; Cl 26.51; S 7.88%. Calculated for C₆H₉Cl₃OS: C 18.13; F 43.02; Cl 26.76; S 8.07%.

Bis-(α -carbomethoxyhexafluoroisopropyl) Disulfide (VIII). A sample of 3.21 g methanol in 10 ml CCl₄ was added dropwise with stirring to a solution of 24.56 g disulfide (III) in 30 ml CCl₄, heated at reflux for 2 h and then fractionated to yield 14.95 g (62%) disulfide (VIII), bp 124-125°C (3 mm), np^{2°} 1.3960. ¹⁹F NMR spectrum: --13.50 s (CF₃). PMR spectrum:

3.85 s (CH_s). IR spectrum: 1760 cm⁻¹ (C=0). Found: C 24.70; H 1.17; F 46.87; S 13.00%. Calculated for C10H6F12O4S2: C 24.90; H 1.26; F 47.28; S 13.30%.

Reaction of Methyl 2-Hydrohexafluoroisobutyrate with Sulfur Chlorides. a) A solution of 10.3 g triethylamine in 10 ml ether and then 6.75 g SC1 were added dropwise with stirring to a solution of 21.0 g methyl 2-hydrohexafluoroisobutyrate in 30 ml dry ether cooled to 0-5°C. The reaction mass was slowly warmed and maintained for 2 h at 20°C and then filtered. The filtrate was fractionated to yield 19.3 g (80%) disulfide (VIII), bp 125°C (13 mm), n_D²⁰ 1.3960. ¹⁹F NMR spectrum: -13.50 s (CF₃). PMR spectrum: 3.85 s (CH₃). IR spectrum: 1760 cm⁻¹ (C=0). Found: C 24.82; H 1.12; F 46.92; S 13.05%. Calculated for C₁₀H₆F₁₂O₄S₂: C 24.90; H 1.26; F 47.28; S 13.30%.

b) A sample of 5.8 g (96%) disulfide (VIII), bp 126-127°C (15 mm), n_D^{20} 1.3958 was obtained under the conditions of the preceding experiment from 10.5 g methyl 2-hydrohexa-fluoroisobutyrate, 5.7 g triethylamine, and 2.6 g SCl₂. ¹⁹F NMR spectrum: -13.50 s (CF₃). PMR spectrum: 3.85 s (CH₃). IR spectrum: 1760 cm^{-1} (C=0).

Phenyl α -Chlorocarbonylhexafluoroisopropyl Sulfide (IX). a) A sample of 9.0 g hexafluorodimethylketene was bubbled into a solution of 7.3 g phenylsulfenyl chloride in 10 ml dry acetonitrile with stirring and cooling to from -5° to 0°C, stirred for 3 h at 0°C and then for 3 h at 20°C. The mixture was fractionated to yield 15.1 g (93%) sulfide (IX), by 90-92°C (13 mm), np^{2°} 1.4677. ¹⁹F NMR spectrum: 14.25 s (CF₃). IR spectrum: 1780 cm⁻¹ bp (C=0) [14].

b) A mixture of 7.3 g phenylsulfenyl chloride, 9.0 g hexafluorodimethylketene, and 10 ml dry SO2 was maintained in a sealed ampul for two days, cooled, and the reaction mass was fractionated to yield 14.9 g (92%) disulfide (IX), bp 90-92°C (13 mm), np²⁰ 1.4680.

CONCLUSIONS

1. The geometry, energy and electronic characteristics were calculated for ketene, dimethylketene, and hexafluorodimethylketene. Substituent effects on the electronic structure of the cumulene group C=C=0 were elucidated and approaches were developed for activation of the reactions of hexafluorodimethylketene with sulfur chlorides and sulfenyl chlorides by specific solvation of the reagents.

2. A necessary condition for the reactions of hexafluorodimethylketene with sulfur chlorides and sulfenyl chlorides is specific solvation of the S-Cl bond of the sulfur chlorides and sulfenyl chlorides. The solvent activating effects are enhanced with increasing donor properties of such solvents.

3. Experimental evidence was found supporting the proposed mechanism for the reactions of hexafluorodimethylketene with sulfur chlorides and sulfenyl chlorides.

LITERATURE CITED

- 1. S. N. Shkurak, A. F. Kolomiets, and A. V. Fokin, Zh. Org. Khim., <u>18</u>, 1519 (1982).
- 2. I. L. Knunyants and A. V. Fokin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 705 (1955).
- 3. I. L. Knunyants and É. G. Bykhovskaya, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 852 (1955).
- 4. G. F. Il'in, A. F. Kolomiets, and G. A. Sokol'skii, Zh. Vses. Khim. Obshch. im. D. I. Mendeleeva, 27, 347 (1982). 5. G. F. Il'in, S. N. Shkurak, A. F. Kolomiets, and G. A. Sokol'skii, Zh. Vses. Khim. Obshch.
- im D. I. Mendeleeva, 28, 235 (1983).
- 6. A. V. Fokin and A. F. Kolomiets, Izv. Akad. Nauk SSSR, Ser. Khim., 1820 (1982).
- 7. L. P. Rasteikene, D. I. Greichute, M. G. Lin'kova, and I. L. Knunyants, Usp. Khim., 46 1041 (1977).
- 8. A. V. Fokin and A. F. Kolomiets, The Chemistry of Thiiranes [in Russian], Izd. Nauka, Moscow (1978).
- 9. A. Roe and J. W. McCechee, J. Am. Chem. Soc., 70, 1662 (1948).
- 10. F. Sorm, J. Smrt, and J. Beranek, Chem. Listy, 49, 573 (1955).
- 11. A. Kistinson, Tetrahedron Lett., 4489 (1973).
- 12. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4899, 4907 (1977).
- 13. M. J. S. Dewar and H. S. Rzepa, J. Am. Chem. Soc., 100, 58 (1978).
- 14. Yu. V. Zeifman, L. T. Lantseva, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2640 (1978).

15. V. Gutman, The Chemistry of Coordination Compounds in Nonaqueous Solvents [Russian] translation], Mir, Moscow (1971).

SYNTHESIS OF NITRONES OF THE POLYFLUOROAROMATIC SERIES

N. I. Petrenko, T. N. Gerasimova, and

UDC 542.943:547.574.4

E. P. Fokin

Nitrones are a reactive and intensively investigated class of compounds [1-4] however polyfluoroaromatic nitrones have not been obtained up to the present time with the exception of α, α -diphenyl-N-pentafluorophenylnitrone in [5].

In the present work the possibility has been investigated of obtaining polyfluoro-substituted α, α, N -triarylnitrones by the oxidation of anils of polyfluoroaromatic ketones which were synthesized by the method developed by us previously in [6, 7].

It is known that Schiff bases are oxidized by peracids forming nitrones as a result of electrophilic interaction of the reagent with the unshared pair on the nitrogen atom, or more frequently forming oxaziridines by orthogonal attack at the carbon atom of the azomethine bond. In those cases when such attack is sterically hindered the reaction forming nitrones predominates [8-10].

It was found by us that the anil of decafluorobenzophenone (Ia) was stable to the extended action of AcOOH in CH_2Cl_2 at $\sim 20^{\circ}C$. The interaction of the same anil (Ia) with CF_3CO_3H under these conditions led to the formation of α, α -bis(pentafluorophenyl)-N-phenylnitrone (IIa) in good yield. Similar results were obtained on oxidizing substituted anils of decafluorobenzo-phenone and also the anil of perfluoro-p-tolylketone (Ig).

 $\begin{array}{c} ({\rm Ar}_{\rm F})_2{\rm C} = {\rm NAr} \xrightarrow[{\rm CF_6C0_{3H}}]{} ({\rm Ar}_{\rm F})_2{\rm C} = {\rm NAr} \\ ({\rm Ia} - {\rm g}) & \downarrow \\ & ({\rm II} \, a - {\rm g}), \ 70 - 80\% \\ {\rm Ar}_{\rm F} = {\rm C}_6{\rm F}_5, \ {\rm Ar} = {\rm Ph} \ ({\rm a}); \ {\rm Ar}_{\rm F} = {\rm C}_6{\rm F}_5, \ {\rm Ar} = {\rm o} - {\rm MeC}_6{\rm H}_4 \ ({\rm b}); \\ {\rm Ar}_{\rm F} = {\rm C}_6{\rm F}_5, \ {\rm Ar} = {\rm p} - {\rm MeC}_6{\rm H}_4 \ ({\rm c}); \ {\rm Ar}_{\rm F} = {\rm C}_6{\rm F}_5, \ {\rm Ar} = {\rm o} - {\rm SO}_6{\rm H}_4 \ ({\rm d}); \\ {\rm Ar}_{\rm F} = {\rm C}_6{\rm F}_5, \ {\rm Ar} = {\rm p} - {\rm MeC}_6{\rm H}_4 \ ({\rm e}); \ {\rm Ar}_{\rm F} = {\rm Ar} = {\rm C}_6{\rm F}_5 \ ({\rm f}); \\ {\rm Ar}_{\rm F} = {\rm p} - {\rm CF}_3{\rm C}_6{\rm F}_4, \ {\rm Ar} = {\rm Ph} \ ({\rm g}). \end{array}$

Compound (If), the nucleophilicity of the nitrogen in which is significantly reduced as a result of the acceptor influence of the pentafluorophenyl group, was oxidized more slowly than the remaining anils of type (I), however nitrone (IIf) was formed in high yield in this way. At the same time the anils of 2,3,4,5,6-pentafluorobenzophenone (IIIa, b) containing one pentafluorophenyl residue on the C=N bond interacts with CF_3CO_3H less unequivocally and gave the corresponding nitrones (IVa, b) in lowest yield



Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1378-1384, June, 1984. Original article submitted May 10, 1983.