SYNTHESIS OF HALOGEN-CONTAINING AZA AND DIAZA DIENE DERIVATIVES OF POLYFLUORO AROMATIC COMPOUNDS

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Previously we showed that the reaction of polyfluoro aromatic amines with CCl_4 and compounds containing a CCl_3 group in the aromatic ring, in particular, with benzotrichloride and pentafluorobenzotrichloride, in the presence of $AlCl_3$ is a new convenient method for the synthesis of polyfluoro aromatic imidolyl chloride derivatives [1]. In the present paper, it was determined that in this reaction compounds with a CCl_3 group at the C=C bond give chlorine-containing aza diene derivatives of polyfluoro aromatic compounds in good yields. Thus, when pentafluoroaniline (I) is heated with perchloropropylene (II) or 2fluoropentachloropropylene (III) in the presence of excess $AlCl_3$, the corresponding aza dienes (IV) and (V) are formed. The reaction of (I) with cis-1-(pentafluorophenyl)-2-fluorotetrachloropropylene (VI) gives a mixture of isomeric aza dienes (VII) with cis and trans orientation of the halogen atoms with respect to the C=C bond (2:3 according to ¹⁹F NMR).



The formation of the trans isomer together with the cis isomer can be explained by a change of the configuration in intermediate cationoid species formed during the reaction in the presence of $AlCl_3$ because starting compound (VI) and cis isomer (VII) do not isomerize under the reaction conditions.

The structure of (VII) was confirmed by ¹⁹F NMR spectral data and the results of hydrolysis. A comparison of the values of the long-range spin-spin coupling constants of the F atom at the aliphatic C=C bond in the isomers of (VII) and in polyfluorinated styrenes [2] makes it possible to assign the cis and trans isomers of (VII). As was to be expected for imidolyl chlorides [3], the corresponding amides were formed in the hydrolysis of (VII) in an aqueous dioxane solution of K_2CO_3 . The corresponding amide (VIII) was recovered and characterized in the case of the trans isomer of (VII), whereas amide (IX), formed from the cis isomer of (VII), apparently underwent intramolecular cyclization rather facilely. The product of this cyclization was recovered from the reaction mixture together with the unreacted starting compound. According to analytical and spectral characteristics, it was assigned the structure of 1-(pentafluoropheny1)-4-chloro-3,5,6,7,8-pentafluoro-2-quinolinone (X). The IR spectrum of (X) contained an intense band of C=O at 1710 cm⁻¹. A band similar in position was observed for the analog 1-methyl-3,4,5,6,7,8-hexafluoro-2-quinolinone [4]. A comparison of the ¹⁹F NMR spectra of these compounds also favored the structure of (X) if we take into account the possible weak-field shift of the ¹⁹F signals in (X) (especially in the 3 position) under the effect of Cl and C_6F_5 (e.g., cf. the difference in the chemical shifts of the β F atoms in perfluorostyrene [5] and α -chloroheptafluorostyrene [6])

trans-(VII)
$$\xrightarrow{K_5CO_5} C_6F_5NHCOCF = CClC_6F_5$$

(VIII)

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2,3-Diaza diene (XII) and azine (XIII) were obtained in the reaction of pentafluorobenzaldehyde hydrazone (XI) with CCl_4 and $AlCl_3$.



Azine (XIII) was identified with the azine described in [7], formed from (XI) in the presence of $AlCl_3$ without the participation of CCl_4 .

EXPERIMENTAL

The IR spectra of solutions of the substances in CCl_4 or $CHCl_3$ were recorded on a UR-20 spectrometer (layer thickness 0.4 mm), and the ¹⁹F and ¹H NMR spectra of the solutions in CCl_4 were recorded on a Varian A56/60A spectrometer (56.4 and 60 MHz) from internal standards of C_6F_6 and hexamethyldisilane (HMDS). The UV spectra of solutions in EtOH were recorded on a Specord UV-VIS instrument. The molecular weights were determined on a Finnigan MAT-8200 high-resolution GC/MS mass spectrometer.

The starting compounds (II), (III), and (XI) were obtained according to [8], [9], and [7], and (VI) was obtained by the reaction of perfluoroallylbenzene with $AlCl_3$ in CCl_4 .*

<u>Reactions of (I) and (XI) with CCl₃ Derivatives in the Presence of AlCl₃</u>. The trichloromethyl derivative was added with vigorous stirring to a suspension of ground freshly sublimed AlCl₃ in an appropriate solvent, and then (I) or (XI) was added, and the whole was heated with vigorous stirring, cooled, poured onto ice, and extracted with ether [CHCl₃ in the reaction with (XI)]. The organic layer was dried with MgSO₄, the solvents were driven off, and the residue was distilled in vacuo (method A) or separated on a column with SiO₂ (125-140 μ m for the isomers of (VII) and 125-315 μ m for the remaining ones, and the eluent was hexane, with a weight ratio of the reaction mixture and silica gel of 1:40) (method B). The reaction conditions and the methods for recovery of the products are given in Table 1.

 $\frac{\text{cis-1,3-Dichloro-2-fluoro-1,4-bis(pentafluorophenyl)-4-aza-1,3-butadiene (VII)}{g (33\%), bp 135-138°C (10 mm). IR spectrum (v, cm⁻¹): 1660 (N=C), 1530 (C_6F_5), 1000 (C-F). UV spectrum [<math>\lambda_{max}$, nm (log ϵ)]: 214 (4.29), 271 (4.02). Fluorine-19 NMR spectrum (δ , ppm): 12.9 (2F₀')+, 4.8 (F_p'), 0.7 (2F_m'), 24.1 (2F₀), 12.6 (F_p), 1.6 (2F_m), 64.0 t (=CF, J_{CF-F_0} = 2 Hz). Found, %: C 37.43; C1 14.69; F 44.02; N 3.08; M 473. C₁₅Cl₂F₁₁N. Calculated, %: C 37.97; Cl 14.98; F 44.09; N 2.95; M (³⁵Cl) 473.

^{*}The procedure was developed by K. V. Dvornikova, Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. +Here and in what follows, the prime denotes fluorine atoms of the C_6H_5 group bonded to the

N atom of the N=C bond.

TABLE 1

Compound with NH ₂ group, g (mmoles)	CCl ₃ deriva- tive, g (mmoles)	AlCl ₃ , g (mmoles)	Solvent, ml	т, с	Time, h	Recovery method
$\begin{array}{c} (I), \ 0.5 \ (2.7) \\ (I), \ 0.4 \ (2.2) \\ (I), \ 0.2 \ (1.1) \\ (XI), \ 1.3 \ (6.2) \\ (XI), \ 0.2 \ (0.9) \end{array}$	(II), 1.02 (4) (III), 0.76 (3) (VI), 0.6 (1.6) CCl ₄ , 20 ml	1,09 (8) 0,88 (6,6) 0,44 (3) 2,48 (18,6) 0,38 (2,8)	C ₆ F ₆ , 8 CHCl ₃ , 10 CHCl ₃ , 5 CHCl ₃ , 5	70-80 50-60 60-65 60-65 60-65	6 6 10 10	B A B B

trans-1,3-Dichloro-2-fluoro-1,4-bis(pentafluorophenyl)-4-aza-1,3-butadiene (VII).

Yield: 0.23 g (44%), bp 160-162°C (10 mm). IR spectrum (ν , cm⁻¹): 1660 (N=C), 1530 (C₆F₅), 1000 (C-F). UV spectrum [λ_{max} , nm (log ε)]: 213 (4.17), 270 (4.13). Fluorine-19 NMR spectrum (δ , ppm): 14.0 (2F₀'), 4.4 (F_p'), 0.4 (2F_m'), 25.4 (2F₀), 12.9 (F_p), 1.9 (2F_m), 60.3 t (=CF, J_{CF-F} = 7 Hz). Found, %: C 37.95; Cl 14.98; F 44.30; N 2.88; M 473. C₁₅Cl₂F₁₁N. Calculated, %: C 37.97; Cl 14.98; F 44.09; N 2.95; M (³⁵Cl) 473.

<u>Hydrolysis of cis-(VII)</u>. A solution of 0.4 g of cis-(VII) in 1 ml of dioxane was added to 2 ml of a 20% aqueous K_2CO_3 solution, the whole was stirred for 1.5 h at 80°C, cooled, extracted with ether, and dried with CaCl₂, and the solvents were driven off. The residue was chromatographed on a column with SiO₂ of 125-140 µm [the eluent was hexane followed by a hexane:ether mixture (4:1)]. We obtained 0.1 g of the starting (VII) and 90 mg (20%) of 1-(pentafluorophenyl)-4-chloro-3,5,6,7,8-pentafluoro-2-quinolinone (X), mp 165.5-167°C (hexane). IR spectrum (ν , cm⁻¹): 1710 (C=O), 1640 (C=C), 1490, 1520 (C₆F₅), 1000 (C-F). UV spectrum [heptane, λ_{max} , nm (log ε)]: 228 (4.23), 242 (4.15), 269 (3.89), 281 (3.90), 292 (3.85), 325 (3.42). Fluorine-19 NMR spectrum [tetrahydrofuran (THF), δ , ppm]: 17.6 (2F₀), 12.4 (F_p), 1.2 (2F_m), 41.6 (F₃), 23.3; 12.6; 11.0; 2.4. Found: M 434.9517. C₁₅ClF₁₀NO. Calculated: M (³⁵Cl) 434.9508.

<u>Hydrolysis of trans(VII)</u>. A solution of 0.37 g of trans-(VII) in 1 ml of dioxane was added to 2 ml of a 20% aqueous K_2CO_3 solution, the whole was stirred for 2 h at 100°C, cooled, extracted with ether, and dried with CaCl₂, and the solvents were driven off. We obtained 0.15 g (43%) of α -fluoro- β -chloropentafluorocinnamic pentafluoroanilide (VIII), mp 132-134°C (aqueous alcohol). IR spectrum (ν , cm⁻¹): 3420 (NH), 1720 (C=O), 1510, 1530 (C₆F₅), 1000 (C-F). PMR spectrum (THF, δ , ppm): 10.2 s (NH). Fluorine-19 NMR spectrum (THF, δ , ppm): 18.6 (2F₀'), 6.0 (F_p'), -0.5 (2F_m'), 25.0 (2F₀), 12.2 (F_p), 1.8 (2F_m), 51.6 t (=CF, J_{CF-Fo} = 7 Hz). Found: M 454.9576. C₁₅HClF₁₁NO. Calculated: M (³⁵Cl) 454.9571.

<u>Investigation of the Possibility of Isomerization of cis-(VI) and cis-(VII)</u>. a) To a suspension of 0.15 g of AlCl₃ in 2 ml of CHCl₃, 0.2 g of cis-(VI) in 0.5 ml of CHCl₃ was added with stirring, the whole was heated for 6 h at 60°C, cooled, poured onto ice, and extracted with ether, the organic layer was dried with MgSO₄, and the solvent was driven off. We obtained 0.2 g of a residue, which, according to ¹⁹F NMR spectral data, contained only the starting cis-(VI).

b) To a suspension of 0.1 g of $AlCl_3$ in 1 ml of $CHCl_3$ was added 0.11 g of cis-(VII) in 1 ml of $CHCl_3$. According to ¹⁹F NMR spectral data, only the starting cis-(VII) was contained in the reaction mixture after stirring (at 60°C for 6 h) and similar treatment.

CONCLUSIONS

l. Halogen-containing aza diene derivatives of polyfluoro aromatic compounds were obtained by reactions of pentafluoroaniline with haloolefins containing a CCl_3 group at the C=C bond in the presence of AlCl₃.

2. A mixture of cis and trans aza dienes is formed by pentafluoroaniline with cis-l-(pentafluorophenyl)-2-fluorotetrachloropropylene in the presence of AlCl₃. 3. 1,6-Dichloro-4-(pentafluorophenyl)-2,3-diaza-1,3-butadiene is formed by pentafluorobenzaldehyde hydrazone with CCl₄ in the presence of AlCl₃.

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ISOMERIC TRANSFORMATIONS OF PERFLUORO-1-VINYL- AND PERFLUORO-

1,3-DIVINYLINDANES BY THE ACTION OF SbF₅ and CsF

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Perfluorinated alkylindenes and alkylideneindanes may be of interest, for example, in the investigation of the influence of fluorine atoms on the properties of aromatic and antiaromatic systems [1]. At present, only perfluoro-2- [2, 3] and perfluoro-3-methylindenes (I) and perfluoro-1-methyleneindane (II) [4] are known, whereof indene (I) was obtained by isomerization of compound (II) by the action of CsF [4]. In this connection, in order to obtain the perfluorinated derivatives of ethylideneindane and ethylindene, we studied the behavior of the recently synthesized [5] perfluoro-1-vinyl- (III) and perfluoro-1,3-divinyl-indanes (IV) under the action of CsF and SbF₅.

Through the action of CsF at 250°C and in the absence of a solvent, indane (III) gives an equilibrium mixture of E- and Z-perfluoro-1-ethylideneindanes (V) and (VI) together with perfluoro-3-ethylindene (VII). From the individual compounds (III), (V)-(VII) practically equivalent mixtures are obtained.

The transformation of compounds (III), (V)-(VII) by the action of CsF can be represented as an addition-elimination of fluoride ion via the intermediate formation of anions (VIII) and (IX) (see scheme top of following page).

Decrease in temperature leads to a decrease in the content of compound (VII) and increase in the amount of (V) in the reaction mixture. The data at $\sim 20^{\circ}$ C were obtained with a solution in MeCN, since in the absence of a solvent, the reaction does not proceed.

When SbF_5 is used as the catalyst, a mixture of compounds (V) and (VI) is obtained from vinylindane (III) at -20°C, in a ratio of 2:1. This mixture does not contain indene (VII). The latter appears when the temperature is increased to ~20°C. On prolonged holding at ~20°C, compounds (V)-(VII) are formed in approximately the same amounts as from a mixture, enriched with indene (VII). It should be noted that mixtures obtained at ~20°C, as a result of prolonged holding with SbF_5 in the absence of a solvent and those obtained

*Deceased.

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