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THE REACTION OF PENTAFLUOROPHENYLTRIMETHYLSILANE

WITH PERFLUORINATED INTERNAL AZAALKENES IN THE

PRESENCE OF CESIUM FLUORIDE

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Pentafluorophenyltrimethylsilane reacts with perfluorinated internal azaalkenes in the presence of cesium fluoride in acetonitrile.

In previous work [1, 2], we showed that pentafluorophenyltrimethylsilane (I) is capable of phenylating polyfluoroolefins in the presence of CsF. In the present work, this reaction was extended to perfluoroazaalkenes. A convenient synthesis of such azaalkanes has recently been reported [3].

Perfluoro-3-aza-2-pentene (II) and perfluoro-5-aza-4-nonene (III) react with silane (I) in the presence of anhydrous cesium fluoride in acetonitrile even at room temperature to give perfluorinated phenylazaalkenes (IV) and (V), respectively, with satisfactory yields.

These compounds, similarly to starting azomethines (II) and (III), are anti isomers as indicated by ¹⁹F NMR spectroscopy. Thus, the signals for the difluoromethylene group attached to the nitrogen atom (b) in the spectra of (II) and (III) appear as a doublet or doublet of triplets, respectively. The doublet coupling constants are 20-21 Hz (compare with the spectrum of perfluoro-2-pentene [4]).

The signal for this difluoromethylene group in the $^{19}{\rm F}$ NMR spectrum of (IV) appears as a triplet with coupling constant 3.5 Hz, corresponding to the reaction of the CF₂-N= group with the ortho-fluorine atoms of the aromatic ring. Analogous behavior is observed for azomethine (V). In the case of syn arrangement of the R_F and R_F' groups, the signal for CF₂(b) would have a coupling constant of about 20 Hz, due to interaction with fluorine atoms (c) or (d) in (IV) or (V), respectively [5].

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 923-924, April, 1990. Original article submitted May 15, 1989. Thus, the geometry of the starting azaalkene remains unchanged during the nucleophilic substitution of the vinyl fluorine atom in azomethines (II) and (III) by a pentafluorophenyl group using silane (I). This may indicate steric specificity of this reaction.

EXPERIMENTAL

The ¹⁹F NMR spectra were taken on a Bruker WP-200 SY spectrometer in $CDCl_3$ with CF_3CO_2H as the external standard. The IR spectra were taken on a Specord IR-75 spectrometer. The mass spectra were taken on a VG-7070F mass spectrometer at 70 eV. The source temperature was 150°C.

Reaction of Silane (I) with Perfluoro-3-aza-2-pentene. A mixture of 2.4 g (10 mmoles) silane (I), 3.0 g (13 mmoles) azomethine (II), 6 ml anhydrous acetonitrile, and 1.6 g freshly roasted CsF was stirred in a flask equipped with a reflux condenser, cooled with dry ice, at 20-22°C for 4 h. Then, the reaction mass was poured onto ice. The lower layer was separated, washed with water, dried over CaCl₂, and distilled to give 2.4 g (63%) (III), bp 131-132°C. ¹⁹F NMR spectrum: 10.1 t (a), 27.3 t (b), -1.5 t (c), 61.5 (ortho), 72.7 (para), and 84.8 (meta); $J_{b-ortho} = 3.5$, $J_{a-ortho} = 2.5$, $J_{c-ortho} = 6$ Hz. IR spectrum in CCl₄: 1711 (C=N), 1653, 1509, 1437 (C₆F₅, C=C), 1335, 1296, 1235, 1177, 1132, 1076, 1000, 859 cm⁻¹. Mass spectrum (m/z, assignment, intensity, %):381 (M⁺, C₁₀F₁₃N⁺, 16.5), 362 (M⁺-F, C₁₀F₁₂N⁺, 10.7), 312 (M⁺ -CF₃, C₉F₁₀N⁺, 38.1), 193 (C₇F₅N⁺, 7.8), 119 (C₂F₅⁺, 100), 69 (CF₃⁺, 50.4). The ions given comprise 86% of the total ion current. The linked scanning method (constant B/E) indicated the following metastable transitions related to the abovementioned ions: $M^+-CF_3 \rightarrow (M^+-CF_3) - C_6F_5CN \rightarrow C_2F_5^+$, $C_2F_5^+-CF_2 \rightarrow CF_3^+$ (M⁺-F) \rightarrow (M⁺-CF₃). Found: C, 31.5; F, 64.8; N, 3.66%. Calculated for C₁₀F₁₃N: C, 31.5; F, 64.8; N, 3.67%.

Reaction of Silane (I) with Perfluoro-5-aza-4-nonene. By analogy to the previous procedure, 4.8 g (20 mmoles) (I), 1.8 g (18.5 mmoles) (III), 0.5 g (3 mmoles) cesium fluoride, and 6 ml acetonitrile gave 6.5 g (56%) (IV), bp 84-86°C (10 mm). ¹⁹F NMR spectrum: 4.1 (a), 22.0 (b), 3.0 (c), 35.8 (d), 48.0 (e,f), 49.0 (e,f), 59.5 (ortho), 69.6 (para), 82.6 (meta); $J_{c-d} = 8$, $J_{b-ortho} = 4$ Hz. IR spectrum in $CCl_4 (\nu, cm^{-1})$: 1690 (C=N), 1643, 1512, 1495 (C₆F₅, C=C), 1423, 1337, 1310, 1230, 1213, 1127, 1033, 979, 893, 871 cm⁻¹. Mass spectrum (m/z): 581 (M⁺, C₁₄F₂₁N⁺, 8.8), 562 (M⁺-F, C₁₄F₂₀N⁺, 15.9), 412 (M⁺-C₃F₇, 39.9), 219 (C₄F₉⁺, 100), 193 (C₇F₅N⁺, 7.6), 131 (C₃F₅⁺, 18.1), 119 (C₂F₅⁺, 8.7), 69 (CF₃⁺, 100). These comprise 90% of the total ion current. Metastable transitions: M⁺-C₃F₇ \rightarrow (M⁺-C₃F₇), (M⁺-F)-C₃F₆ \rightarrow (M⁺-C₃F₇), (M⁺-F)-(C₁₀F₁₁N \rightarrow C₄F₉⁺, (M⁺-C₃F₇)-C₆F₅CN \rightarrow C₄F₉⁺, (M⁺-C₃F₇), C⁺₆F₅N⁺, (M⁺-C₃F₇)-C₈F₉N \rightarrow C₂F₅⁺, (M⁺-C₃F₆) \rightarrow CF₃⁺, C₃F₅⁺, C₃F₅⁺, C₃F₅⁺, C₃F₅⁺, C₃F₅⁺, C₃F₅⁺, C₃F₅⁺, Found: C, 28.4; F, 68.4; N, 2.42%. Calculated for C₁₄F₂₁N: C, 28.9; F, 68.7; N, 2.41%.

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