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REACTION OF O-TRIPHENYLPHOSPHIMINOFORMYLISOBUTYROHYDROXIMOYL CHLORIDE WITH HEXAFLUOROACETONE

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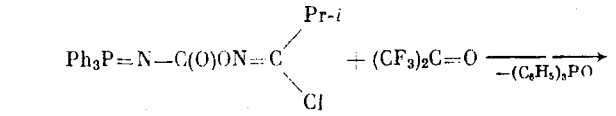
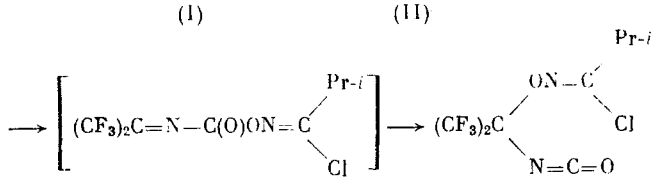
UDC 542.91:547.558.1+547.415.3:547.446.5'161

O-Triphenylphosphiminoformylisobutyrohydroximoyl chloride reacts with hexafluoroacetone to give the product of a sigmatropic rearrangement, namely, α-(O-isopropylchloroformimino)hexafluoroisopropyl isocyanate.

Phosphazo compounds react with perfluoroketones to form the corresponding N-substituted imine derivatives, including N-carbalkoxy derivatives [1]. Thus, we might have expected that treatment of O-triphenylphosphiminoformylisobutyrohydroximoyl chloride (I) with hexafluoroacetone (HFA) (II) would give the corresponding HFA imine (III). However, isocyanate (IV) was the only fluorine-containing product. The formation of (IV) is apparently related to the 1,3-sigmatropic rearrangement of (III) due to the presence of the electron-withdrawing oxime group at the carbonyl carbon atom. The nucleophilic properties of this oxime group are the driving force for this isomerization.



(I) (II)

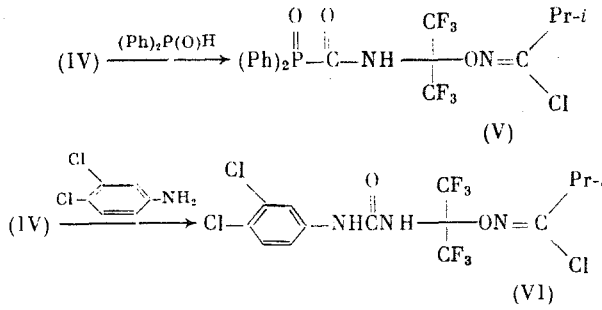


(III) (IV)

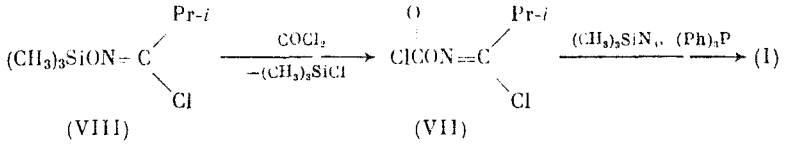
The structure of (IV), which was synthesized in our previous work by a different method [2], was supported by IR and NMR spectroscopy and some chemical transformations. Thus, (IV) reacts exothermally with diphenylphosphonous acid and 3,4-dichloroaniline to give the corresponding phosphine oxide (V) and urea (VI).

Institute of Physiologically Active Compounds, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1921-1923, August, 1991. Original article submitted November 20, 1990.

 0568-5230/91/4008-1708$12.50



Starting phosphimine (I) was obtained by the reaction of triphenylphosphine with chloroformylisobutyrohydroximoyl chloride (VII) in the presence of trimethylsilyl azide. In turn, (VII) was formed in 81% yield upon heating trimethylsilylisobutyrohydroximoyl chloride (VIII) with phosgene.



Thus, we have shown that the Staudinger reaction may be used not only for the synthesis of imines of perfluoroketones but also for the synthesis of α-substituted perfluoroalkyl isocyanates, containing electron-withdrawing groups in the α-position.

EXPERIMENTAL

The ^1H, ^{19}F, and ^{31}P NMR spectra were obtained on a Bruker CXP-200 spectrometer in $CDCl_3$ solutions.

O-(Triphenylphosphiminoformyl)isobutyrohydroximoyl Chloride (I). A sample of 5.75 g (0.05 mole) trimethylsilyl azide was added with stirring to a solution of 4.2 g (0.05 mole) (VII) and 13.1 g (0.05 mole) triphenylphosphine in 100 ml ether at 20°C. The reaction mixture was stirred until nitrogen was no longer evolved and then filtered. The residue was recrystallized from benzene to give 15.6 g (73.5%) (I), mp 128-130°C. Found: C, 65.38; H, 5.14; N, 6.37%. Calculated for $C_{23}H_{22}ClN_2O_2P$: C, 65.02; H, 5.22; N, 6.59%. PMR spectrum (δ, ppm): 1.2 d (6H, $2CH_3$, J = 7 Hz), 3.04 m (H, CH), 7.32-7.90 m (15H, $3C_6H_5$). ^{31}P NMR spectrum: δ = 23.8 ppm.

α-(O-Isopropylchloroformimino)hexafluoroisopropyl Isocyanate (IV). A mixture of 21.2 g (0.05 mole) (I) and 8.3 g (0.05 mole) (II) in 50 ml ether in a sealed ampul was agitated for 12 h and then filtered. The filtrate was evaporated and fractionated to give 10.8 g (69.1%) (IV), bp 144-146°C, n_D^{20} 1.3840. PMR spectrum (δ, ppm): 1.25 d (6H, $2CH_3$, J = 7 Hz), 2.70 m (H, CH). ^{19}F NMR spectrum (δ, ppm): -0.88 s. IR spectrum (ν, cm^{-1}): 1600 (C=N), 2250 (N=C=O).

N-α-(O-Isopropylchloroformimino)hexafluoroisopropyl-diphenylphosphinylformamide (V). A sample of 3.12 g (0.01 mole) (IV) in 10 ml ether was added with stirring to a solution of 2.02 g (0.01 mole) diphenylphosphonous acid in 100 ml ether at 20°C. The reaction mixture was stirred for 1 h. Ether was evaporated. The residue was recrystallized from hexane to give 4.2 g (82%) (V), mp 69-71°C. PMR spectrum (δ, ppm): 1.04 d (6H, $2CH_3$, J = 7 Hz), 2.65 m (H, CH), 7.55 m (6H, $2C_6H_5$), 7.88 m (4H, $2C_6H_5$), 8.75 s (H, NH). ^{19}F NMR spectrum (δ, ppm): 3.28 s. ^{31}P NMR spectrum: δ = 17.63 ppm. Found: C, 46.91; H, 3.57; N, 5.50; P, 6.16%. Calculated for $C_{20}H_{18}ClF_6N_2O_3P$: C, 46.66; H, 3.52; N, 5.44%.

N-α-(O-Isopropylchloroformimino)hexafluoroisopropyl-N-3,4-dichlorophenylurea (VI). A sample of 3.12 g (0.01 mole) (IV) in 15 ml ether was added with stirring to a solution of 1.62 g (0.01 mole) 3,4-dichloroaniline in 20 ml ether at 20°C. The reaction mixture was stirred for 1 h. Ether was evaporated and the residue was recrystallized from hexane to give 3.0 g (63.3%) (VI), mp 121-122°C. PMR spectrum (δ, ppm): 1.2 d (6H, CH_3, J = 7 Hz) 2.88 m (H, CH), 7.36 m (2H, C_6H_5), 7.54 (H, C_6H_5), 7.84 d (H, NH, J = 1.5 Hz), 8.1 s (H, NH). ^{19}F NMR spectrum (δ, ppm): 4.22 s. Found: C, 35.70; H, 2.58; N, 8.45%. Calculated for $C_{14}H_{12}Cl_3F_6N_3O_2$: C, 35.42; H, 2.55; N, 8.85%.

O-(Chloroformyl)isobutyrohydroximoyl Chloride (VII). A mixture of 19.3 g (0.1 mole) (VIII) and 10.0 g (0.1 mole) phosgene was heated in a sealed ampul for 3 h at 70-80°C and then $(CH_3)_3SiCl$ was distilled off. The residue was fractionated to give 14.9 g (81.3%) (VII), bp 62-64°C (7 mm), n_D^{20} 1.4600. PMR spectrum (δ, ppm): 2.28 d (6H, $2CH_3$, J = 7 Hz), 4.03 m (H, CH). Found: C, 32.71; H, 3.84; N, 7.73%. Calculated for $C_5H_7Cl_2NO_2$: C, 32.64; H, 3.83; N, 7.61%.

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CIS EFFECT IN THE NUCLEOPHILIC SUBSTITUTION OF CYCLOTRIPHOSPHAZENES

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UDC 530.145:541.6:547.1'118

Semiempirical CNDO/2 calculations have provided an interpretation for the observed cis effect in the nucleophilic replacement of cyclotriphosphazenes.

Nucleophilic replacement in cyclophosphazenes most often proceeds through a geminal mechanism. However, if the nucleophile is, for example, a bulky amine, geminal replacement does not occur and the reaction may lead to a cis or trans isomers (Fig. 1).

In a detailed experimental study, Keat and Shaw [1] have shown that the aminolysis of hexachlorocyclotriphosphazene in such cases most often leads to the trans isomer of $N_3P_3Cl_4(NR_2)_2$. The predominant formation of this isomer could not be attributed to steric factors upon the examination of molecular models [2]. Keat and Shaw [3] have named this phenomenon the "cis effect" and proposed an interpretation. The amino group is capable of transferring electrons preferentially to the nongeminal cis chlorine atom, thereby enhancing the negative charge of this atom and reducing this direction for attack of the nucleophile. Thus, the negatively charged nucleophilic agent attacks the phosphazene molecule from the opposite side of the molecule and adds to the trans position.

In order to check this proposal, we carried out semiempirical CNDO/2 calculations for monosubstituted cyclophosphazenes $N_3P_3Cl_5X$ (X = F, OMe, NH_2, Me, Ph) using different bases. The VIKING program package was used for the calculations [4].

The calculations in the sp and standard spd bases show the lack of a cis effect (Table 1).

These same compounds were calculated in the spd' basis with optimization of exponential indices of the phosphorus 3d atomic orbital (AO). In this optimization, the Slater exponent of the phosphorus 3d AO is selected for the most correct representation of these orbitals starting from the criterion of a total molecular energy minimum [5] since the radial part of the d orbitals is taken to be dependent on the electron properties of the substituents at the phosphorus atom.

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1924-1925, August, 1991. Original article submitted December 18, 1990.

0568-5230/91/4008-1710$12.50