A NEW METHOD OF SYNTHESIZING 1,1,3-TRIPHENYL-1H-ISOINDOLE

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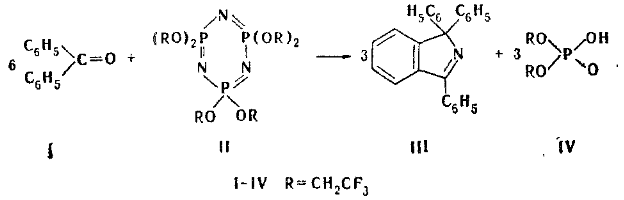
It has been shown that the reaction of benzophenone with 2,2,4,4,6,6-hexakis-(2,2,2,-trifluoroethoxy)-1,3,5,2,4,6-triazatriphosphorin gives as the main reaction products 1,1,3-triphenyl-1H-isoindole and di(2,2,2-trifluoroethyl)phosphate.

In studying the reaction of benzophenone (I) with 2,2,4,4,6,6-hexakis-(2,2,2-trifluoroethoxy)-1,3,5,2,-4,6-triazatriphosphorin (II) we found that heating the reaction mixture (molar ratio 6 : 1) at 220-230°C led to the formation of 1,1,3-triphenyl-1H-isoindole (III) and to di(2,2,2-trifluoroethyl)phosphate (VI) as the main reaction products.



The reaction of (I) with 2,2,4,4,6,6,8,8-octakis(2,2,2-trifluoroethoxy)-1,3,5,7,2,4,6,8-tetraazatetraphosphorin $[NP(OCH_2CF_3)_2]_4$ (V) took place similarly.

According to the results of elementary analysis, melting point, and IR and UV spectra, the compound (III) that we synthesized (yield 63-71%) accurately corresponds to 1,1,3-triphenyl-1H-isoindole, which has been described previously [1]. Its PMR spectrum lacks the signals of aliphatic protons. An intense peak with m/e 345.15 in the mass spectrum corresponds to the molecular ion $(C_{26}H_{19}N)^{+\circ}$, mol. wt. 345.45.

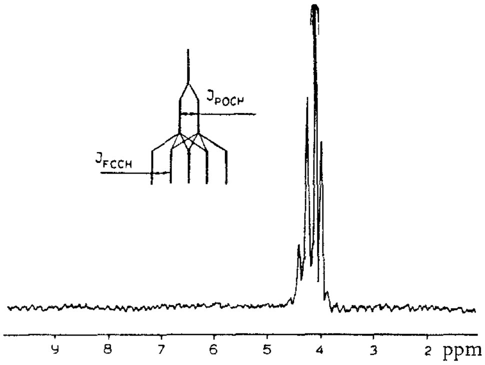


Fig. 1. PMR spectrum of di(2,2,2-trifluoroethyl)-phosphate.

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In the PMR spectrum (Fig. 1), the methylene protons of compound (IV) appear in the form of a quintet (δ 4.13 ppm). The formation of a quintet is explained by the spin–spin coupling of the methylene protons with the magnetic ^{19}F and ^{31}P nuclei. The spin–spin coupling constants $^3J_{FH} = {}^3J_{PH} = 7.6$ Hz. The resonance peak of the hydroxy proton is in the very-low-field region and has a chemical shift of δ 12.93 ppm. The chemical shift of the phosphorus appears at 8 ppm relative to 85% H_3PO_4.

EXPERIMENTAL

The PMR spectra were recorded on an RYa-2303 instrument with a working frequency of 60 MHz using tetramethylsilane as internal standard, and the ^{31}P NMR spectra on a YaMR-KGU-4 instrument with a working frequency of 10.2 MHz.

Reaction of (I) and (II). a) A mixture of 15 g (0.02 mole) of (II) and 23 g (0.12 mole) of (I) was heated in a sealed tube at 220-230°C for 60 h, and the resulting viscous dark-brown resin was boiled with 700 ml of water under reflux for 3 h. Then the hot aqueous solution was separated from the insoluble part of the reaction product, and the residue after evaporation was distilled in vacuum. This gave (IV) (yield not considered) in the form of a colorless oil with bp 105°C (0.05 mm), n_D^{20} 1.3361, d_4^{20} 1.6159. Found, %: C 18.4; H 2.0; P 11.8; MR_D 33.63. $C_4H_5F_6O_4P$. Calculated %: C 18.3; H 1.9; P 11.8; MR_D 33.86.

The dark-brown water-insoluble crystalline mass, after drying in the air, was recrystallized several times from n-hexane. This gave 13.5 g (63.4%) of (III) in the form of colorless crystals with mp 146-147°C. According to the literature [1], mp 145.5°C.

b) A reaction product obtained as described above was washed from the tube with 250 ml of hot 2% NaOH and was boiled in this solution for 1 h. The alkaline solution was decanted from the insoluble brown residue, neutralized with conc. HCl, and then evaporated in vacuum. The pulverulent mass obtained (20.7 g) was treated with several portions of dry ether (total amount ~100 ml). After the ether had been distilled off, 9.0 g of a white paraffin-wax-like substance was obtained (mp 245°C, decomp.), the IR spectrum of which was identical with that of sodium di(2,2,2-trifluoroethyl) phosphate.* Repeated recrystallization from petroleum ether of the water-insoluble reaction component gave 14.0 g (65.7%) of (III) with mp 146.5-147°C.

c) A mixture of 21 g (0.11 mole) of (I) and 14 g (0.02 mole) of (II) was heated in a sealed tube at 220-225°C for 60 h. The dark-brown resin formed was dissolved in benzene and chromatographed on a column of Al_2O_3, elution being performed with benzene–carbon tetrachloride (9 : 1). This gave 10.4 g (52.3%) of (III), mp 145-147°C (from petroleum ether).

In an analogous experiment, with 10.1 g (0.01 mole) of (V) and 16.2 g (0.09 mole) of (I), chromatography yielded 10.2 g (71.5%) of (III), mp 145-146°C.

LITERATURE CITED

1. W. Theilacker, H. J. Bluhm, W. Heitmann, H. Kalenda, and H. J. Meyer, Ann. Chem., 673, 96 (1964).

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*A sample of the salt was provided by Dr. M. Bond (J. Birkbeck College, University of London).