PHOSPHINIMINOFUROXANES: SYNTHESIS AND OXIDATION TO DIAZENE OXIDE DERIVATIVES

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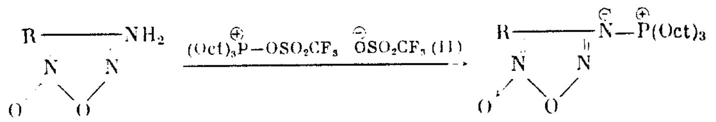
The reaction of 4-aminofuroxanes with trioctylphosphine bis-triflate gave 4-trioctylphosphinimine derivatives, whose oxidation leads to the first reported furoxanyldiazene oxides.

In previous work [1], we synthesized sulfyliminofuroxanes and showed that both nitro and nitroso derivatives may be obtained by oxidation. In a continuation of this work, it would be logical to study the behavior of other furoxane imines upon oxidation.

In the present work, we synthesized 4-trioctylphosphiniminofuroxanes and studied their oxidation. In order to obtain phosphiniminofuroxanes, we studied the reaction of 4-aminofuroxanes with trioctylphosphine bis-trifluoroacetate (I) and bis-triflate (II). The latter has been used for the synthesis of phosphiniminofurazanes [2].

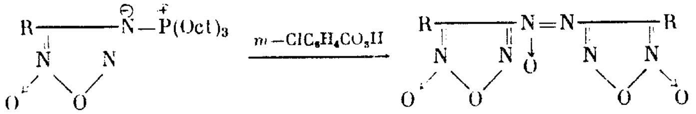
We have shown that (I) does not react with 4-amino-3-phenyl- (III) and 4-amino-3-methylfuroxanes (IV). Upon using (II), both aminofuroxanes form phosphinimino derivatives (V) and (VI) in 57% yield.



R = Ph (III), (V); CH_3 (IV), (VI).

A 2.2-fold molar excess of (II) is required for the complete conversion of the amine as in the preparation of sulfyliminofuroxanes [1]. The relatively low yields of phosphiniminofuroxanes may be attributed to decomposition of (V) and (VI) formed in the reaction medium by the action of excess (II).

The first furoxanyldiazene oxides, namely, bis(3-phenylfuroxanyl)diazene 1-oxide (VII) (obtained in 79% yield) and bis(3-methylfuroxanyl)diazene 1-oxides (VIII) (obtained in 82% yield) were obtained upon the oxidation of phosphinimines (V) and (VI) by m-chloroperbenzoic acid.



R = Ph (V), (VII); CH_3 (VI), (VIII).

Oxides (VII) and (VIII) are yellow compounds, whose structure was indicated by elemental analysis, NMR spectroscopy, and mass spectrometry.

EXPERIMENTAL

The IR spectra were taken for KBr pellets on a Specord spectrometer. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz relative to TMS. The mass spectra were taken on a Varian MAT CH-6 mass spectrometer. The ^{13}C and ^{14}N NMR spectra were taken on a Bruker AM-300 spectrometer at 75.5 and 21.6 MHz, respectively, relative to TMS as an internal standard and nitric acid as an external standard. Thin-layer chromatography was carried out on Silufol UV-254 plates.

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4-Trioctylphosphinimino-3-phenylfuroxane (V). A solution of 1.18 g (4.2 mmoles) $(CF_3SO_2)_2O$ and 3 ml CH_2Cl_2 was added dropwise to a solution of 1.62 g (4.2 mmoles) Oct_3PO in 5 ml CH_2Cl_2 at -5°C and maintained for 30 min at this temperature. Then, a solution of 0.34 g (1.9 mmoles) (III) in a mixture of 3 ml CH_2Cl_2 and 2 ml acetonitrile was added. The reaction mixture was maintained at -20°C for 2.5 h, cooled to 0°C, and treated with 5 ml saturated aqueous Na_2CO_3. The organic layer was separated, washed with two 3-ml portions of water, dried over $MgSO_4$, and evaporated. The residue was subjected to chromatography on a column packed with silica gel (L 100/160μ) with chloroform as the eluent to give 0.59 g (57%) (V) as a yellow, oily liquid, R_f 0.80 (chloroform). Found: C, 70.24; H, 10.11; N, 7.65; P, 5.32%. Calculated for $C_{32}H_{56}N_3O_2P$: C, 70.46; H, 10.28; N, 7.71; P, 5.69%. Mass spectrum, m/z: 545 (M^+). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm): 156.17 (C=N), 107.36 (C=N(O)), 124.96, 123.62, 122.60, 121.25 (Ph), 37.25, 26.88, 24.24, 20.51, 19.39, 17.73, 24.60, 9.64 (C_8H_{17}).

Analogously, 0.52 g (57%) (VI) was obtained as a colorless oil, R_f 0.67 (chloroform). Found: C, 67.31; H, 10.88; N, 8.75; P, 6.31%. Calculated for $C_{27}H_{54}N_3O_2P$: C, 67.08; H, 11.18; N, 8.70; P, 6.42%. Mass spectrum, m/z: 483 (M^+). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm): 161.10 (C=N), 11.30 (C=N(O)), 6.80 (H_3CC=N), 31.32, 21.04, 30.35, 28.50, 23.99, 22.20, 21.28, 13.56 (C_8H_{17}).

Bis(3-phenylfuroxanyl)diazene 1-Oxide (VII). A solution of 0.55 g (1 mmole) (V) in 8 ml dichloroethane was added dropwise to a solution of 0.27 g (1.5 mmoles) m-chloroperbenzoic acid in 5 ml dichloroethane. The reaction mixture was maintained at 70°C for 1 h and cooled to 0°C. m-Chloroperbenzoic acid was filtered off and the filtrate was treated with 5 ml saturated aq. $NaHCO_3$. The organic layer was separated, washed with two 3-ml water portions, and dried over $MgSO_4$. After evaporation of the solvent, the residue was subjected to chromatography on a column packed with silica gel 100/160μ with 1:2 hexane–chloroform as the eluent to give 0.14 g (79%) (VII), mp 190-192°C (from methanol), R_f 0.57 (1:2 hexane–chloroform). Found: C, 52.67; H, 2.71; N, 22.65%. Calculated for $C_{16}H_{10}N_6O_5$: C, 52.46; H, 2.75; N, 22.94%. Mass spectrum, m/z: 366 (M^+). PMR spectrum* in $(CD_3)_2SO$ (δ, ppm): 7.47 m, 7.71 m (1 OH, C_6H_5). ^{13}C NMR spectrum* in $(CD_3)_2SO$ (δ, ppm): 158.11, 154.35 (C=N), 111.06 (C=N(O)), 131.22, 130.72, 129.47, 128.73, 128.66, 127.64, 121.05, 120.69 (Ph). ^{14}N NMR spectrum in $(CD_3)_2SO$ (δ, ppm): 70.1 (N=N(O)).

Analogously, 0.1 g (82%) (VIII) was obtained, mp 187-189°C (chloroform), R_f 0.52 (1:2 hexane-chloroform). Found: C, 29.91; H, 2.59; N, 34.47%. Calculated for $C_6H_6N_6O_5$: C, 29.76, H, 2.50; N, 34.71%. Mass spectrum, m/z: 242 (M^+). PMR spectrum* in $(CD_3)_2SO$ (δ, ppm) 2.49 s (3H(CH_3)), 2.23 s (3H(CH_3)). ^{13}C NMR spectrum* in $(CD_3)_2SO$ (δ, ppm): 159.35, 155.76 (C=N), 110.10, 109.77 (C=N(O)), 9.92, 7.80 (Me). ^{14}N NMR spectrum in $(CD_3)_2SO$ (δ, ppm), -66.9 (N=N(O)).

LITERATURE CITED

1. O. A. Rakitin, O. G. Vlasova, L. F. Chertanova, and L. I. Khmel'nitskii, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1020 (1990).
2. M. D. Coburn, J. Heterocycl. Chem., 23, 421 (1986).
3. L. I. Khmel'nitskii, T. I. Godovikova, N. A. Ruleva, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2295 (1979).

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*The signals of the atoms of the substituents bound to the –N(O)= fragment of the diazene oxide group are found at lower field [3].