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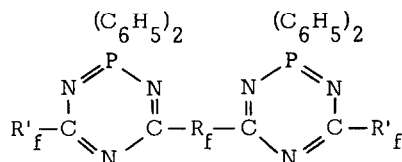
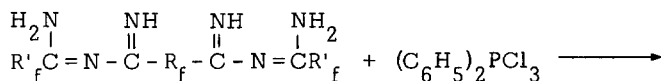
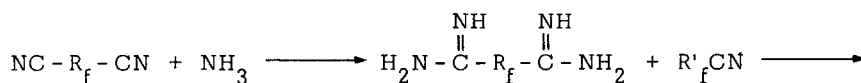
SHORT COMMUNICATION

Phospha-s-triazines. V. Synthesis of Dumbbell Compounds

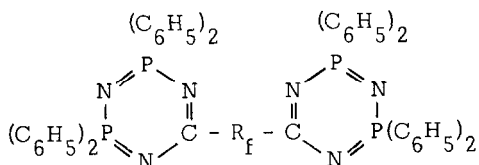
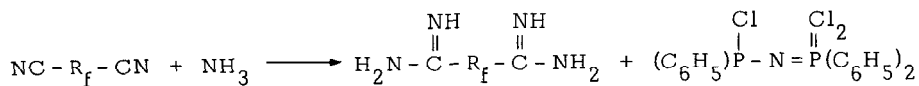
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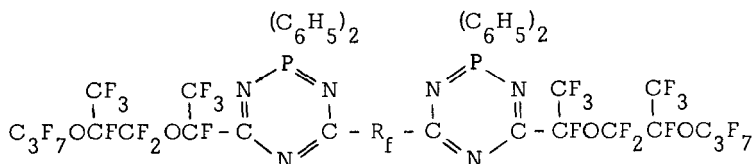
To obtain materials possessing the desired properties exhibited by the earlier described [1,2] monophospha- and diphospha-s-triazines and to attain at the same time increased molecular weight and thus reduced volatility in an essentially monomeric system free of end-group effects, dumbbell analogues were synthesized. The synthesis of the monophospha-s-triazine dumbbell analogues can be illustrated by the following scheme:



The diphospha-s-triazine terminated analogue was synthesized by the following reaction sequence:



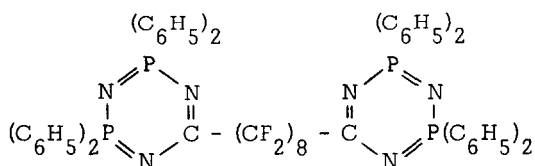
The three specific compounds thus prepared are depicted below:



Compound I, $\text{R}_f = -(\text{CF}_2)_8-$

Compound II, $\text{R}_f = -\text{CF}(\text{CF}_3)[\text{OCF}_2\text{CF}(\text{CF}_3)]_m\text{O}(\text{CF}_2)_5\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF}(\text{CF}_3)-$

$$m + n = 3$$



Compound III

As would be expected, the two monophospho-s-triazines I and II containing perfluoroalkylether substituents on the ring carbon atoms were liquids at room temperature, even when the bridging group was a perfluoroalkyl moiety as in Compound I. The dumbbell diphospho-s-triazine, Compound III, in agreement with the results obtained for the single ring analogues, was a solid, mp 168-169°C.

Preparation of Perfluorosebacodiamidine

To liquid ammonia (15 ml) at -40°C was added perfluorosebaconitrile [3] (5.02 g, 11.10 mmol) over a period of 20 min. The solution was then stirred at -28°C for 1 hr. After warming to room temperature and ammonia removal, pure perfluorosebacodiamidine (5.37 g, 99.4% yield), mp $175-178^{\circ}\text{C}$, was obtained. This material was insoluble in refluxing common solvents, including Freon-113. The mass and infrared spectra were found to be consistent with the structural arrangement.

Preparation of Perfluoroalkyl, Perfluoroalkylether imidoylamidine, $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)-\text{CF}_2\text{OCF}(\text{CF}_3)\text{C}(\text{NH}_2)=\text{N}-\text{C}(=\text{NH})(\text{CF}_2)_8\text{C}(=\text{NH})-\text{N}=\text{C}(\text{NH}_2)\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$

To perfluorosebacodiamidine (2.03 g, 4.18 mmol) was added the ether nitrile, $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{CN}$, (6.13 g, 12.85 mmol) and the mixture was stirred at room temperature for 5 days; subsequently, the excess of nitrile (2.34 g, 4.91 mmol, 96% reaction) was removed in vacuo. The product (5.81 g, 96.7% yield; at the end of one day the reaction extent was only 54.5%) exhibited infrared and mass spectra consistent with the assigned structure.

Preparation of Dumbbell-monophospha-s-triazine, Compound I (n.c.)

A mixture of the imidoylamidine, $[\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{C}(\text{NH}_2)=\text{N}-\text{C}(=\text{NH})_2(\text{CF}_2)_8]$, (3.00 g, 2.08 mmol) and diphenyltrichlorophosphorane (1.40 g, 4.80 mmol) was heated under nitrogen by-pass for 259 hr at $99-107^{\circ}\text{C}$. Subsequently, the product was dissolved in Freon-113 and purified by filtration through a 1.5 x 3.5 cm column of Woelm neutral alumina. The viscous liquid thus obtained (2.20 g, 59% yield) was found by GC to consist of 94% of the dumbbell triazine, 4% of monophospha-s-triazine, $[(\text{C}_6\text{H}_5)_2\text{PN}][\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)-\text{CF}_2\text{OCF}(\text{CF}_3)\text{CN}]_2$, and 2% of unidentified products. Anal. Calcd. for $\text{C}_{52}\text{H}_{20}\text{F}_{50}\text{N}_6\text{O}_4\text{P}_2$: C, 34.61; H, 1.12; F, 52.64; N, 4.66; P, 3.43; MW, 1804. Found: C, 34.72; H, 0.98; F, 54.35; N, 4.75; P, 3.42; MW, 1800.

Preparation of Dumbbell-monophospha-s-triazine, Compound II (n.c.)

A mixture of the bis-imidoylamidine, $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(NH_2)=N-C(=NH)]_2[CF(CF_3)(OCF_2CF(CF_3))_mO(CF_2)_5O(CF(CF_3)CF_2O)_nCF(CF_3)]$, 3.96 g, 1.96 mmol), which was prepared following the procedure of Anderson and Psarras [4], and diphenyltrichlorophosphorane (1.28 g, 4.39 mmol) was stirred and heated under nitrogen by-pass for 185.5 hr at 103-117°C. The product mixture was dissolved in Freon-113 and purified by filtration through a 1.5 x 3.5 cm column of Woelm neutral alumina. The solvent was removed in vacuo and the residue (2.83 g, 49.4% yield) was dried at 100-110°C for 13 hr. Anal. Calcd. for $C_{62}H_{20}F_{70}N_6O_9P_2$: C, 31.23; H, 0.85; F, 55.77; N, 3.52; P, 2.60; MW, 2384. Found: C, 32.06; H, 1.13; F, 54.36; N, 3.77; P, 3.04; MW, 1850. The low molecular weight found is due to the presence of a small quantity of 1-diphenylphospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine produced via the reaction of diphenyltrichlorophosphorane with the monoimidoylamidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)-N=C(NH_2)CF(CF_3)-OCF_2CF(CF_3)OC_3F_7$, which is invariably formed [2] as a by-product in the preparation of the amidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)NH_2$, the reactant required for the production of the above-depicted bis-imidoylamidine.

Preparation of Dumbbell-diphospha-s-triazine, Compound III (n.c.)

Under nitrogen by-pass to a stirred solution of imido-tetraphenyl-diphosphinic acid trichloride [5] (1.66 g, 3.38 mmol) in *s*-tetrachloroethane (15 ml) at 98°C was added perfluorosebacodiamidine (0.82 g, 1.69 mmol) over a period of 11 min. Heating at 94-101°C was continued over a period of 185 hr. The residue obtained on removal of the solvent was tritiated with Freon-113 and the Freon-113 soluble portion was then treated with hot *n*-heptane. The insoluble material was redissolved in Freon-113 and filtered through a 1.5 x 3.5 cm column of Woelm neutral alumina. The material thus obtained was crystallized from a Freon-113/acetone/pentane solvent mixture to give a white powder, mp 168-169°C. Anal. Calcd. for $C_{58}H_{40}F_{16}N_6P_4$: C, 55.78; H, 3.23; F, 23.34; N, 6.73; P, 9.93. Found: C, 55.79; H, 3.57; F, 23.10; N, 6.61; P, 10.36. Due to the insolubility of the pure compound in common organic solvents, including hexafluorobenzene, the molecular weight could not be determined.

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- 3 Sample was kindly provided by Mr. W. R. Griffin, U.S. Air Force Materials Laboratory.
- 4 R. Anderson and T. Psarras, Development of High Temperature Functional Fluids, AFML-TR-71-208 (November 1971).
- 5 E. Fluck and F. L. Goldmann, *Chem. Ber.*, 96, 3091 (1963).