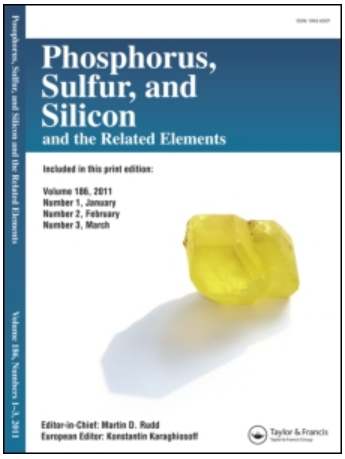

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SYNTHESIS OF A PHOSPHORUS- AND NITROGEN-CONTAINING BIS-ADDUCT WITH MALEIC ANHYDRIDE

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SYNTHESIS OF A PHOSPHORUS- AND NITROGEN-CONTAINING BIS-ADDUCT WITH MALEIC ANHYDRIDE

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A new phosphorus- and nitrogen-containing bis-adduct was synthesized through the interaction between maleic anhydride and a phosphorus-, nitrogen- and difuryl-containing compound by the Diels–Alder reaction. The adduct was isolated and characterized through analytical methods. The structure of the compound was studied by means of IR- and ^{1}H-NMR-spectroscopy. The endo-configuration has been established for the bis-adduct.

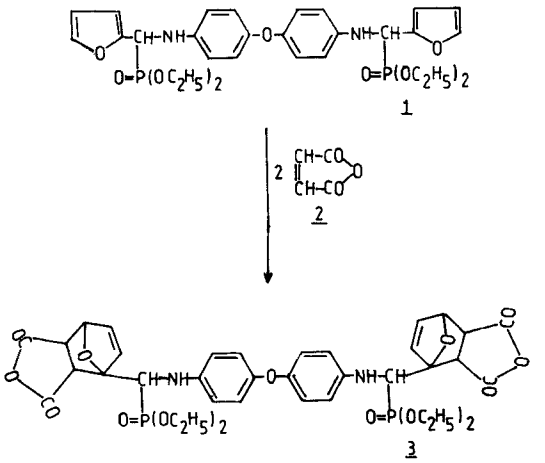
INTRODUCTION

It is known[1] that most furan-containing compounds are functioning as active dienes, interacting with dienophiles. The formation of stable adducts of furan and bis-furan derivatives and maleic anhydride, maleimide, aromatic dimaleimides and other dienophiles by Dields–Alder reaction has been reported.[2,3,4] Some of the synthesized bis-adducts have been dehydrated by means of an acid with the aim to obtain aromatic structures.[3,5] These compounds are suitable monomers for the synthesis of thermal stability heterocyclic polymers.[6] In this respect the synthesis of similar phosphorus-containing bis-adducts is of considerable interest. These adducts can be used as monomers in the synthesis of polymers, because of their polyfunctional properties. It may be expected that the introduction of phosphorus into the polymer molecules, together with other valuable properties, should reduce the flammability of these products.[7]

RESULTS AND DISCUSSION

A phosphorus- and nitrogen-containing bis-adduct **3** has been prepared in the reaction of a phosphorus-, nitrogen- and difuryl-containing compound **1** and

maleic anhydride **2**, according to the following scheme:



The reaction was conducted at 70°C in benzene (molar ratio diene:dienophile = 12.6). From the reaction mixture 4,4'-bis{N-methyl(diethoxyphosphonyl)-1-[4,10-dioxa-3,5-dioxo-tricyclo/5,2,1,0/ec-8-en-1-yl]} diaminodiphenyl ether was isolated (m.p. 169°C; %P: calc. = 7.49, found = 7.59; %N: calc. = 3.38, found = 3.10). The yield of the product was high—86.3%. The partial and total acid numbers of the dianhydride were determined and were in agreement with the theoretical values (acid number: partial—calc. = 135.5, found = 129.5; total—calc. = 271.0, found = 272.4).

The electrophilic reagent, maleic anhydride, attacks the electronegative α-carbon atoms of the furan rings and the addition takes place in the usual 1,4-position of the furan rings as well as is known for other furan-containing compounds.[2,3] It is known[1,8,9] that the presence of electrophilic substituents at the side chain of the furan ring may impede the addition of the dienophile. Our results indicate that the electron-attracting phosphorus-containing substituent $(C_2H_5O)_2P=O$ at the α-carbon atom of the side chain of the furan ring does not interfere with the interaction of maleic anhydride and the phosphorus-, nitrogen- and difuryl-containing compound **1**.

The structure of the bis-adduct **3** was confirmed by IR- and ^{1}H-NMR-spectroscopic data. In the IR-spectrum of the compound absorption bands typical of the furan ring of the starting difuryl-containing compound **1** (760, 880, 962 cm^{-1}) have not been observed. Absorption bands due to a C=O group and C=C bond were observed at 1710 and 1665 cm^{-1}. Absorption bands were ascribed to the P=O (1250 cm^{-1}), P—OC_2H_5 (1160 cm^{-1}), NH (3400 $^{-1}$).

The ^{1}H-NMR-spectroscopic data of the bis-adduct **3** also confirm the proposed structure. The presence of a bicyclic ring is indicated by the doublets observed at 3.20 and 2.79 ppm, with a corresponding vicinal coupling constant of 9.30 Hz. It is known[10] that endo-endo vicinal coupling constants are smaller than exo-exo vicinal coupling constants in such bicyclic adducts. The observed vicinal coupling constant is an indication of an exo-exo configuration of both protons, H-2 and H-6. This is in agreement with the expected formation of an endo-adduct, as

obtained by us. The signals shifted downfield at 6.82 and 6.45 ppm are due to the protons, H-8 and H-9 of the cycle. The value of the observed vicinal coupling constant ($^3J = 6.03$ Hz) is typical for cis-oriented olefinic protons. The presence of a slight broad singlet at 5.17 ppm is ascribed to H-7. A symmetrical multiplet, shifted downfield, indicated an AA'BB' spin system, caused by a para-dissubstituted benzene ring. A doublet at 7.34 ppm, with $^3J = 8.18$ Hz is ascribed to the ortho-H, with respect to the O-atom, and a doublet is centered at 6.88 ppm, and $^3J = 8.13$ Hz, for the ortho-H, with respect to the N-atom. The doublet at 4.82 ppm with $^2J = 5.60$ Hz, due to spin couplings with the ^{31}P-nucleus, is assigned to the CH(P)-proton. The signals at 4.09 and 3.97 ppm are observed as complex multiplets, because of spin interaction with the ^{31}P-nucleus. The latter signals correspond to the CH_2-protons of the ethoxy group. The signal of the NH-protons is in the same region. The two triplets, shifted upfield (at 1.18 and 1.12 ppm, with $^3J = 7.31$ Hz, $^3J = 6.87$ Hz) are due to the CH_3-protons. The observed chemical non-equivalence for the CH_3- and CH_2-protons of the CH_3CH_2O group almost certainly results from the asymmetric carbon centre in the molecule. On the basis of the spectral parameters the product obtained should be in the endo-configuration. In the ^{1}H-NMR-spectrum of the reaction mixture remaining after removing the main product was established the presence of a minor amount of the diastereoisomeric bis-adduct, with the exo-configuration.

In the ^{1}H-NMR spectrum of the endo-product signals for furan ring protons are absent. This observation indicates that the diene synethesis between maleic anhydride **2** and the phosphorus-, nitrogen- and difuryl-containing compound **1** to be complete.

EXPERIMENTAL

Starting compounds: the phosphorus-, nitrogen- and difuryl-containing compound (PNDF), was obtained through the addition of diethyl phosphite to N,N'-bis(furfurylidene)diaminodiphenyl ether according to Reference 11, m.p. 165°C; maleic anhydride m.p. 54°C. The melting points were determined on a Kofler microscope. The acid numbers (partial and total) were determined, following Reference 12–14. The infra-red spectrum was recorded on a UR-20 sepectrophotometer (KBr disc). The FT NMR-spectrum was taken on a Bruker WM-250 spectrometer at 250.13 MHz for ^{1}H (5 mm o.d. sample tube) at ambient probe temperature, using TMS as internal reference. $CDCl_3$ was employed as a solvent. Typical instrumental conditions were, memory size, 16 K; pulse width, ca 40°; digital resolution, 0.4 Hz, and number of scans, 256. Spin-decoupling experiments were conducted, to confirm the assignment of the proton signals.

Interaction between PNDF and maleic anhydride. In a flask, fitted with a mechanical stirrer, reflux condensor, thermometer and an aron inlet were placed maleic anhydride (0.52 g, 0.0053 mole) and PNDF (1.3 g, 0.0020 mole). Dry benzene (50 ml) was added and the reaction mixture was refluxed with stirring for 37 h. Then, the benzene was removed by vacuum distillation and the reaction product was purified by precipitating it twice in diethyl either from a solution in dimethylformamide. The product was dried to constant weight in vacuum. The product, 4,4'-bis{N-methyl(diethoxyphosphonyl)-1-[4,10-dioxa-3,5-dioxo-tricyclo/5,2,1,0/ec-8-en-1-yl]} diaminodiphenyl ether, was obtained in 86.3% yield (1.47 g).

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