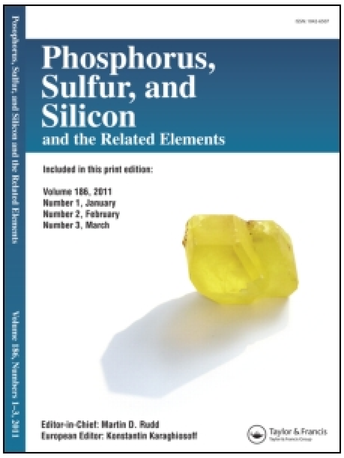

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Kraicheva, I. , Stefanova, R. and Borisov, G.(1993) 'ADDITION PRODUCTS OF MALEIC ANHYDRIDE TO PHOSPHORUS-AND NITROGEN-CONTAINING FURAN DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 79: 1, 107 — 111

To link to this Article: DOI: 10.1080/10426509308034403

URL: http://dx.doi.org/10.1080/10426509308034403

Phosphorus, Sulfur, and Silicon, 1993, Vol. 79, pp. 107–111
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ADDITION PRODUCTS OF MALEIC ANHYDRIDE TO PHOSPHORUS- AND NITROGEN-CONTAINING FURAN DERIVATIVES

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(Received January 26, 1993)

Diels-Alder reaction between maleic anhydride and phosphorus-, nitrogen- and difuryl-containing compounds was carried out giving two new bis-adducts: 1,4-bis{*N*-methyl(diethoxyphosphonyl)-1-[4,10-dioxa-3,5-dioxo-tricyclo[5,2,1,0]ec-8-en-1-yl]}diaminobenzene and 4,4′-bis{*N*-methyl(diethoxyphosphonyl)-1-[4,10-dioxa-3,5-dioxo-tricyclo-[5,2,1,0]ec-8-en-1-yl]}diaminodiphenylmethane. The structure of the compounds was confirmed by Ir-, ^{1}H- and ^{31}P-NMR-spectra. TLC-data are also presented.

Key words: Diels-Alder reaction; maleic anhydride; furan derivatives; phosphonic acid esters; NMR; TLC.

INTRODUCTION

The Diels-Alder reaction is widely used for the synthesis of polyfunctional compounds.[1,2,3,4] Stereochemical studies have been performed in order to clarify the mechanism of the addition.[5,6] The activity of numerous compounds participating in this reaction as dienes or dienophiles has been discussed.[7] Some phosphorus-containing compounds are also found to react according to the Diels-Alder mechanism.[8] Thus, the diethyl ester of *N*-sulphinylphosphoramide has been used as a dienophile in condensation with butadiene.[7] A series of phosphate dienes has been prepared and tested in 4 + 2 cycloaddition reactions with cyclohexenone and maleic anhydride.[9] *Trans*-2-diethyl-phosphoryloxy-1,3-pentadiene has been reacted with α,β-unsaturated ketones to give the corresponding adducts.[10] Diels-Alder adducts of maleic anhydride and other dienophiles and dialkyl-1,3-butadiene-2-yl phosphates have also been described.[11] Some Diels-Alder adducts have been used as monomers for the synthesis of polymers with specific properties.[12,13] Diels-Alder reaction have also been carried out between polymeric chains.[14]

Here we report the synthesis and characterization of two phosphorus- and nitrogen-containing Diels-Alder adducts. They could further be used as monomers for the preparation of polymers with improved thermal stability and flame resistance.

RESULTS AND DISCUSSION

Diels-Alder reaction between the phosphorus-, nitrogen- and difuryl-containing compounds **1** and **2** and maleic anhydride was carried out to give 1,4-bis{*N*-

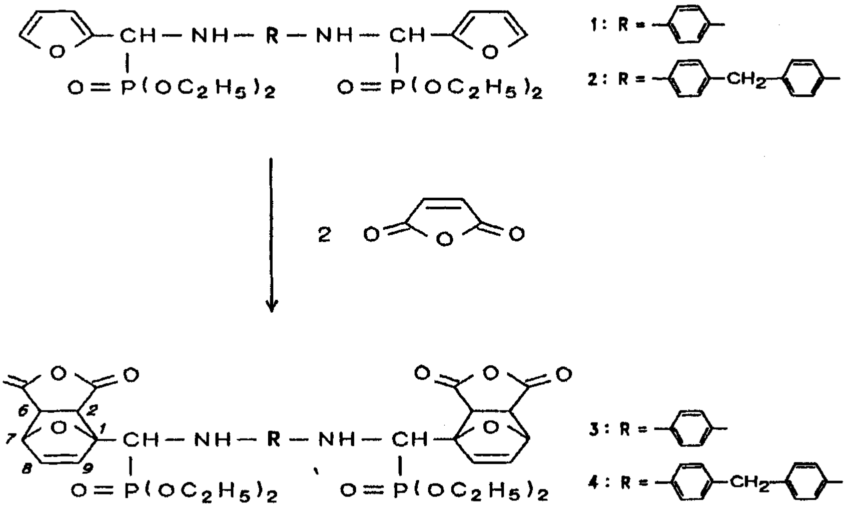
methyl(diethoxyphosphonyl)-1-[4,10-dioxa-3,5-dioxo-tricyclo-[5,2,1,0]-ec-8-en-1-yl]}diaminobenzene **3** and 4,4′-bis{*N*-methyl(diethoxyphosphonyl)-1-[4,10-dioxa-3,5-dioxo-tricyclo-[5,2,1,0]-ec-8-en-1-yl]}diaminodiphenylmethane **4**, respectively, according to Scheme 1.

The starting dienes **1** and **2** were prepared by addition of diethyl phosphite to difuryl-containing Schiff bases.[15] The dienophile component was taken in excess of 30%. The reaction was conducted in benzene at 70°C. Benzene appeared to be a suitable solvent for preparing both adducts due to the possibility to shift the equilibrium into the desired direction.[13] The bis-adducts were isolated in high yields despite the presence of the electron-acceptor phosphorus substituent near the furan ring. The reaction ran however slower as compared to other cases where the phosphorus-containing fragment was absent.[13] Taking into account the literature data,[9,16] this could be explained by the influence of the phosphorus substituent on the electron density in the furan ring and the steric hindrance.

The structure of the synthesized compounds was confirmed by their IR-, ^{1}H- and ^{31}P-NMR-spectra. In the IR-spectra of the adducts the bands corresponding to the stretching vibrations of the following characteristic groups were observed: C=O at 1708 cm^{-1} (**3**) and 1705 cm^{-1} (**4**); P=O at 1267 cm^{-1} (**3**) and 1269 cm^{-1} (**4**); P—OC$_2$H$_5$ at 1160 cm^{-1} (both **3** and **4**); N—H at 3417 cm^{-1} (**3**) and 3421 cm^{-1} (**4**).

Multiplet signals centered at 18.99 ppm and at 19.14 ppm were found in the ^{31}P-NMR-spectra of **3** and **4**, respectively. ^{1}H-NMR-parameters of the compounds studied are presented in Table I. The magnitudes of ^{3}J(H(2)–H(6)) (9.20 Hz and 9.10 Hz for **3** and **4**, respectively) are an indication in support of *endo*-configuration[3,17] of the adducts.

Although both the adducts discussed appeared to be sufficiently pure as indicated by their elemental analyses, acid numbers (partial and total) and NMR-spectra, they exhibited an interesting TLC-behaviour. These compounds gave two elongated diffuse spots of similar intensity, with approximate R_f-values of 0.03 and 0.10. The



SCHEME 1

TABLE I

^{1}H-NMR parameters of **3** and **4**

	Chemical shifts, δ (ppm)										Coupling constants, J (Hz)					
Compound No.	CH_3	CH_2	CH(P)	H(2)	H(6)	H(7)	H(8)	H(9)	Ph	NH	^3J (CH_2—CH_3)	^3J (P—OCH_2)	^2J (P—CH)	^3J (H(2)-H(6))	^3J (H(8)-H(9))	^3J (NH—CH)
3	1.10(t)	4.00(m)	5.30(t)	3.06(d)	2.60(d)	5.00(br.s)	6.70(d)	6.60(d)	7.50(d)	12.20(br.s)	7.10	10.30	6.20	9.20	5.80	6.00
	1.08(t)	3.90(m)									7.00	9.30				
4*	1.07(t)	4.00(m)	4.80(t)	3.20(d)	2.80(d)	5.10(br.s)	6.80(d)	6.40(d)	7.30(d)	12.20(br.s)	7.10	10.30	6.30	9.10	5.80	6.20
	1.05(t)	3.90(m)							7.10(d)		7.12	10.70				

*The signal for the methylene protons of $C_6H_4CH_2C_6H_4$ is at 3.90 ppm (s).

R_f-values became larger with the increase of the concentration of the samples in the layer. A similar picture was observed under the same chromatographic conditions for the previously reported[18] adduct 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, as well as for maleic anhydride. The latter gave two diffuse spots with R_f-values of about 0.10 and 0.30. The above described phenomenon could be explained by decomposition of the compounds on the layer, probably due to the attack of the anhydride ring by water contained in silica gel.[19] Under the same conditions the starting furan-containing compounds **1** and **2** were characterized by one well-shaped spot with R_f-values of 0.55 and 0.58, respectively. The starting diene for preparing 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 gave also one spot with a R_f-value of 0.57.

When examined on a heating-plate polarization microscope, compound **3** exhibited flowing of the solid species at 220°C. Compound **4** began to flow at 140°C. Under cross polaroids, double-refracting structures were observed in the flow drops at 184°C. On the other hand, the thermogravimetric analysis of the same compound indicated that in the interval of 165–190°C the destruction occurs with maximum rate and the sample loses about 14% of its weight. Then the destruction proceeds considerably slower and up to 500°C the total weight-loss of the compound is 42.4%. The effect observed at 184°C is probably due to destruction products which are not a subject of the present work.

EXPERIMENTAL

Starting compounds: **1** and **2** were obtained through the addition of diethyl phosphite to *N,N′*-bis(furfurylidene)-1,4-diaminobenzene and to *N,N′*-bis(furfurylidene)-4,4′-diaminodiphenylmethane, respectively, according to Reference 15, m.p. 204°C (**1**) and 157°C (**2**); maleic anhydride, m.p. 54°C. The melting of the compounds was examined on a Kofler microscope and on a Reichert-Zetopan heating-plate polarization microscope. The acid numbers (partial and total) were determined following References 20, 21, 22. The IR spectra were recorded on a UR-20 spectrophotometer (KBr-disks). ^{1}H- and ^{31}P-NMR-spectra were taken on a Bruker WM-250 spectrometer operating at 250.13 MHz in FT mode at room temperature. ^{1}H-NMR-spectra were recorded in DMSO-d_6 (**3**) and in $CDCl_3$ (**4**) using TMS as an internal reference. ^{31}P-NMR-spectra were taken in DMF (**3**) and in DMSO (**4**) applying 85% H_3PO_4 as an external standard. TLC were performed on Kieselgel 60 F_{254} plastic sheets (Merck). The samples were applied as DMF solutions, with the exception of maleic anhydride which was dissolved in tetrahydrofuran. The chromatograms were developed ascendingly using ethylacetatetetrahydrofuran-methanol (6:3:1) solvent system. The spots were detected under UV light and in iodine vapours. The thermogram was taken on a Paulik-Erdey derivatograph in air at a heating rate of 5°/min.

Preparation of 1,4-bis{N-methyl(diethoxyphosphonyl)-1-[4,10-dioxa-3,5-dioxo-tricyclo-[5,2,1,0]ec-8-en-1-yl]}diaminobenzene (**3**). In a flask, fitted with a mechanical stirrer, reflux condenser, thermometer and an argon inlet were placed maleic anhydride (0.71 g, 0.0072 mol) and **1** (1.50 g, 0.0028 mol). Dry benzene (50 ml) was added and the reaction mixture was refluxed with stirring for 37 h. The benzene was removed by vacuum distillation and the reaction product was purified by precipitating twice in diethyl ether from a solution in DMF. The product was dried to constant weight in vacuum. Yield 86.1% (1.76 g); %P: calc. = 8.42, found = 9.20; %N: calc. = 3.80, found = 3.69; acid number: partial-calc. = 152.2, found = 160.9; total-calc. = 304.4, found = 309.1.

Preparation of 4,4′-bis{N-methyl(diethoxyphosphonyl)-1-[4,10-dioxa-3,5-dioxo-tricyclo-[5,2,1,0]ec-8-en-1-yl]}diaminodiphenylmethane (**4**). This was prepared similarly by reaction of maleic anhydride (1.01 g, 0.0103 mol) and **2** (2.49 g, 0.0040 mol) in benzene (83 ml). The product was purified by precipitating twice in diethyl ether from a solution in tetrahydrofuran. After drying to constant weight in vacuum the yield was 75.5% (2.47 g); %P: calc. = 7.51, found = 7.12; %N: calc. = 3.39, found = 3.75; acid number: partial-calc. = 135.6, found = 140.0; total-calc. = 271.2, found = 297.6.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. L. Minkova for the aid in polarization microscope investigations of the compounds. We also thank the Bulgarian Foundation "Scientific Researches" for the financial support.

REFERENCES

1. W. J. Feast and L. A. Shahada, *Eur. Polym. J.*, **27,** 27 (1991).
2. M. E. Jung and C. A. McCombs, *Tetrahedron Lett.*, **34,** 2935 (1976).
3. R. Cremlyn, F. Swinbourne and R. Nunes, *Phosphorus and Sulfur*, **33,** 65 (1987).
4. J. Sauer, *Angew. Chem.*, **78,** 233 (1966).
5. J. Sauer, *Angew. Chem.*, **79,** 76 (1967).
6. V. Lucchini, M. Prato, G. Scorrano and P. Tecilla, *J. Org. Chem.*, **53,** 2251 (1988).
7. G. Kresze and W. Wucherpfenning, *Angew. Chem.*, **79,** 109 (1967).
8. M. Petrzilka and J. I. Grayson, *Synthesis*, **1981,** 753.
9. T. Calogeropoulou and D. F. Wiemer, *J. Org. Chem.*, **53,** 2295 (1988).
10. H.-J. Liu and W. M. Feng, *Synthetic Commun.*, **16,** 1485 (1986).
11. F. Kienzle and P. Rosen, *Helv. Chim. Acta*, **62,** 442 (1979).
12. H. S. Patel and H. S. Vyas, *Eur. Polym. J.*, **27,** 93 (1991).
13. A. A. Berlin, B. I. Liogonkii, B. I. Zapadinskii, E. A. Kazantseva and A. O. Stankevich, *Vysokomol. Soedin.* Ser. A., 1976, **18,** 926–935; C. A., **85,** 94712p (1976).
14. Y. Chujo, K. Sada and T. Saegusa, *Macromolecules*, **23,** 2636 (1990).
15. I. Kraicheva, B. I. Liogonkii, R. Stefanova and G. Borisov, *Eur. Polym. J.*, **24,** 1167 (1988).
16. F. Sun and R. M. Ottenbrite, *Polymer Preprints*, **32,** 190 (1991).
17. K. Vokac, Z. Samek, V. Herout and F. Sorm, *Collect. Czech. Chem. Commun.*, **34,** 2288 (1969).
18. I. Kraicheva, B. I. Liogonkii, R. Stefanova and G. Borisov, *Phosphorus and Sulfur*, **40,** 145 (1988).
19. E. Knappe and I. Rohdewald, *Fresenius' Z. Anal. Chem.*, **232,** 340 (1967).
20. N. W. Hanson, *Paint Oil Chem. Rev.*, **16,** 16 (1950).
21. W. Klausch, *Farbe und Lack*, **63,** 119 (1957).
22. W. Reiser, Farbe und Lack, **65,** 370 (1959).