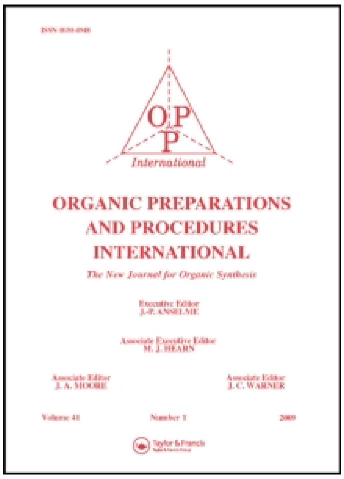

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Bogumil Laszkiewicz[a]; Jacek Dutkiewicz[a]
[a] Politechnika Lodzka, Instytut Wlokien Sztucznych, Lodz, POLAND

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THE EFFECT OF SOME ARYLOXY SUBSTITUENTS ON THE PREPARATION OF ARYLOXY PHOSPHAZENE TRIMERS AND ON THEIR STRUCTURAL CHARACTERISTICS

Bogumil Laszkiewicz* and Jacek Dutkiewicz

Politechnika Lodzka, Instytut Wlokien Sztucznych
90-924 Lodz, POLAND

Dedicated to Professor C.G. Overberger on the Occasion of his 60th Birthday

Although the synthesis of aryloxyphosphazenes by treatment of chlorocyclophosphazene oligomers with sodium arylates is a well known procedure[1-3], it seemed worthwhile to show certain subtleties associated with this reaction. The chemical composition and structure of aryloxyoligocyclophosphazenes have a direct effect on their reactivity, thermal properties and on other physicochemical characteristics. The problem has practical importance since these compounds have potential use as flame-retardant components of polymeric materials.

A series of sodium arylates (ArONa) were allowed to react in acetone solution with hexachlorocyclotriphosphazene (HCP) to determine the effect of the aryloxy substituent on the structural features of the resultant products. The aryloxy groups involved (Table 1) included benzene or naphthalene rings with or without substituent bromine atoms.Table 1 indicates that if the molar ratio of ArONa:HCO is 2.2:1, all the chlorine atoms in a phosphazene molecule can be replaced by phenoxy, p-bromophenoxy, p-cresyl and 2-naphthoxy groups. In the case of sodium salts of 2,4,6-tribromophenol, pentabromophenol, 2,4,6-tribromo-m-cresol and of brominated 2-naphthol (58.8%Br), only three out of the six chlorines in HCP were, on the average, easily substituted with an aryloxy group.

TABLE 1. Data of Arylolysis of HCP

Aryloxy Substituent	Ratio $\frac{(ArONa)}{(NPCl_2)}$	Time (hrs)	Yield[a] (%)	Elemental Analysis[b] C	H	N	P	N^o Cl Substd
C_6H_5O	2.2:1	3	35(A)	61.8 (65.2)	4.4 (4.5)	6.2 (6.3)	13.2 (9.5)	6
p-BrC_6H_4O	2.2:1	3	96(A)	36.9 (37.9)	2.1 (2.1)	3.6 (3.7)	8.0 (5.5)	6
2,4,6-$Br_3C_6H_2O$	1.1:1	3	57(B)	17.6 (17.5)	0.6 (0.5)	3.6 (3.5)	7.5 (5.3)	3
2,4,6-$Br_3C_6H_2O$	1.5:1	3	55(B)	17.5	0.5	3.5	7.6	3
2,4,6-$Br_3C_6H_2O$	2.2:1	10	76(B)	17.3	0.7	3.6	7.3	3
2,4,6-$Br_3C_6H_2O$	3.0:1	10	77(B)	17.5	0.6	3.4	7.5	3
C_6Br_5O	1.1:1	3	48(B)	12.6 (12.9)	0.1 (0.0)	2.8 (2.5)	5.7 (3.8)	3
C_6Br_5O	1.5:1	3	51(B)	12.5	0.2	2.9	5.5	3
C_6Br_5O	2.2:1	10	61(B)	12.7	0.0	2.7	5.9	3
C_6Br_5O	3.0:1	10	65(B)	12.5	0.1	3.0	5.5	3
p-MeC_6H_4O	2.2:1	3	31(A)	68.1 (64.9)	5.7 (5.4)	5.6 (5.4)	12.6 (12.0)	6
2,4,6-Br_3(m-Me)C_6HO	1.1:1	3	47(B)	19.7 (20.2)	0.9 (0.9)	3.2 (3.4)	7.3 (5.1)	3
2,4,6-Br_3(m-Me)C_6HO	1.5:1	3	43(B)	19.9	1.0	3.3	7.2	3
2,4,6-Br_3(m-Me)C_6HO	2.2:1	10	52(B)	19.8	0.9	3.3	7.4	3
2,4,6-Br_3(m-Me)C_6HO	3.0:1	10	59(B)	19.6	0.9	3.1	7.4	3
$C_{10}H_7O$	2.2:1	3	74(B)	71.6 (74.7)	4.2 (4.4)	4.4 (4.4)	9.4 (6.5)	6
$C_{10}H_{7-x}Br_xO$[c]	1.1:1	3	66(B)	27.8	1.1	3.0	7.1	3
$C_{10}H_{7-x}Br_xO$	1.5:1	3	71(B)	27.9	1.1	3.1	7.0	3
$C_{10}H_{7-x}Br_xO$	2.2:1	10	84(B)	28.1	1.3	2.9	6.9	3
$C_{10}H_{7-x}Br_xO$	3.0:1	10	79(B)	28.1	1.0	3.1	7.2	3

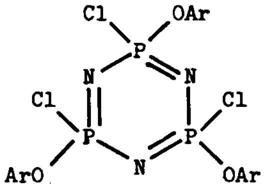
a. Separation procedure (A orB) given in parenthesis. b. Calculated values given in parenthesis. c. Brominated 2-naphtoxy.

The reaction of HCP with the sodium salt of 2,4,6-tribromophenol, pentabromophenol, 2,4,6-tribromo-m-cresol and of brominated 2-naphtol, resulted in pro-ducts whose compositions remained practically unchanged over a range of molar ratios of ArONa to HCP of 1.1:1 and up to 3:1.

Elemental analyses of these derivatives showed that these chlorine atoms were substituted with an aryloxy radical in an HCP molecule.

The first three stages of HCP phenolysis are probably of a non-geminal nature due to the bulkiness of an aryloxy radical. Further replacement of chlorine atoms with ArO groups was feasible under the applied experimental conditions only in the case of smaller substituents, such as of phenoxy, p-bromophenoxy, p-cresyl and of unbrominated naphthoxy. The yields of the reaction between HCP and sodium phenoxylates defined by these aryloxy groups can be correlated with their electronegativity in such a manner that the higher their electronegativity, the higher the yield of the resultant products. This tendency is illustrated by the data presented in Table 1. It is interesting to note that this situation does not hold in the case of bulky substituents such as 2,4,6-tribromophenoxy, pentabromophenoxy, 2,4,6-tribromo-m-cresyl and brominated 2-naphthoxy. In spite of the high electronegativity of these brominated aryloxy groups, the yields of the reaction products are rather low. Presumably such an effect is due in some way to the steric hindrance caused by these substituents on a cyclotriphosphazene molecule.

If a non-geminal pattern in the arylolysis of HCP with bulky arylates is assumed, the formula for the trisubstituted products obtained in this study can be elucidated as follows.



Ar = 2,4,6-$Br_3C_6H_2O$-,
= C_6Br_5O-,
= 2,4,6-Br_3(m-Me)C_6HO-,

The synthesized hexa- and trisubstituted aryloxy derivatives of HCP were characterized by their IR and NMR spectra. The former (Fig. 1) show the absorption bonds characteristic for P-OAr bonds as well as those corresponding to the asymmetric stretching vibrations of the phosphazene cycle. Phosphazene absorption can probably be found in between 1275 and 1230 cm^{-1} in the IR spectrum. The shift of the P-N peaks to higher wave number values with respect to HCP can be correlated approximately with the electronegativity of the aryloxyl substituent in a following way: $p\text{-}MeC_6H_4O < C_6H_5O < p\text{-}BrC_6H_4O < C_{10}H_7O$. The above observation is consistent with the theory of the relationship between the substituent electronegativity and the extent of electron delocalization in the phosphazene trimer. Stretching vibrations of a P-N bond in $[(2,4,6\text{-}Br_3C_6H_2O)ClPN]_3$, $[(C_6Br_5O)ClPN]_3$, $[(2,4,6\text{-}Br_3(m\text{-}Me)C_6HO)ClPN]_3$ and in the brominated 2-naphthoxy derivative appear at lower frequencies despite the fact that the aryloxy substituents linked to phosphorus are more electronegative than the nonphosphorelated phenoxy, cresyl and naphthoxy groups. Such a hypothesis is supported by different degrees of arylolysis in the former and in the latter compounds. The distribution of pi electrons in a cyclotriphosphazene ring becomes a net effect of both unsubstituted chlorine atoms and of aryloxy functions.

The aryloxycyclotriphosphazenes obtained were also characterized by NMR analysis. Their ^1H NMR spectra indicate a close resemblance with the spectra of the respective parent phenols except for the hydroxyl hydrogen signal. As expected, no conjugation is visible between the aryloxy protons and the phosphazene phosphorus since the former are separated from the latter with more than four bonds.

Chemical ^{31}P shifts are shown in Table 2 for the aryloxycyclotriphosphazenes with phenoxy, p-bromophenoxy, p-cresyl and 2-naphthoxy groups. However, no spectra of the remaining products here could be made on a Jeol JNM-C-60-HL spectrometer because of the low solubilities.

TABLE 2. ^{31}P Chemical Shifts for Aryloxycyclotriphosphazenes[a]

Substituent	Solvent	^{31}P Shift Values(d) ppm
C_6H_5O	$CHCl_3$	-8.5
p-BrC_6H_4O	$CHCl_3$	-8.7
p-MeC_6H_4O	$CHCl_3$	-8.5
$C_{10}H_7O$	C_6H_6	-8.9

a. 85% H_3PO_4 as reference.

The (d) values from Table 2 are all higher than that obtained for HCP (-19.3ppm) which is a consequence of stronger shielding of the phosphorus nucleus caused by the aryloxy groups. The increased electron density may be the effect of the substituent electronegativity and of the conjugation of a free pair of electrons on oxygen with an unoccupied d orbital of the P atom.

EXPERIMENTAL

Materials and Methods. - The substrates used for the preparation of aryloxyphosphazenes were hexachlorocyclotriphosphazene obtained according to the procedure described elsewhere,[6] phenol (Chem.Co., Osviecim), p-bromophenol (Reakhim), 2,4,6-tribromophenol (Fluka AG, Buchs SG), pentabromophenol (Berk Ltd.), p-cresol (BDH Chemicals Ltd.) and two arylols prepared as shown below, i.e., 2,4,6-tribromo-m-cresol and brominated 2-naphthol. The IR spectra were run as KBr pellets on a Specord 71 IR spectrometer; ^{1}H NMR analysis of the phenoxy-, p-bromophenoxy-, and p-cresyl derivatives was carried out on a Tesla BS 478-C spectrometer whereas the remaining products were analysed with the aid of a Bruker HFX 90 apparatus. The ^{31}P NMR spectra were obtained using a Jed JNM-C-6 HL spectrometer.

Preparation of 2,4,6-Tribromo-m-cresol.- Bromine (16g, 0.1 mol) was dropped stepwise into m-cresol (13.6 g, 0.1 mol) at ambient temperature and the mixture was stirred for 0.5 hr. A slight vacuum was applied to remove HBr. The product was purified by crystallization from ethanol and dried over P_2O_5 to afford 34.1 g (91.4%) white crystals, mp. 81-82°.

<u>Anal</u>. Calcd for $C_7H_5Br_3O$: C, 24.5; H, 1.4; Br, 69.5.
Found: C, 24.7; H, 1.4; Br, 69.3.

<u>Bromination of 2-Naphthol</u>. - Bromine (64 g, 0.4 mol) was dropped into (14.4 g, 0.1 mol) naphthol dissolved in 200 ml of glacial acetic acid, and the mixture was stirred at 100° for 4 hrs. The HBr formed during that time was removed from the reaction vessel. Unreacted bromine was distilled and the crude product was precipitated with water and purified by dissolution in ethanol followed by precipitation with water. The product was dried over P_2O_5 to afford 34.7 g (91.0%) white crystals, mp. 83-86°.
<u>Anal</u>. Calcd for $C_{10}H_5Br_3O$: C, 31.4; H, 1.4; Br, 62.9.
Found: C, 34.8; H, 1.7; Br, 58.8.

<u>Preparation of Aryloxycyclotriphosphazenes</u>.- Sodium arylates were obtained from the reaction of sodium (2.8 g, 0.12 mol) with the phenol (0.1 mol) in 50 ml of dried acetone. To this mixture was added dropwise a solution of HCP in acetone (50 ml) at 25° over 30 min.; the mixture was then refluxed for various periods of time (Table 1). The products remained in solution or precipitated along with sodium chloride. In procedure (A), they were precipitated with water, filtered and washed repeatedly with water and ethanol to remove unreacted substrates and sodium chloride.In procedure (B), the aryloxyphosphazenes were separated by filtration and washed repeatedly with water and ethanol.

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