Reaction of the Lithium Enolate of Acetaldehyde, Li(OCH=CH_2), with Cyclothiaphosphazenes

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Reactions of the lithium enolate of acetaldehyde, Li(OCH=CH_2), with the mixed ring systems $[NS(O)Ph]_{3-n}(NPCl_2)_n$ (n = 1 or 2) lead to a complete series of vinyloxy derivatives. The vinyloxy group is stable in subsequent substitution reactions using amines as nucleophiles. The compound $[NS(O)Ph]NPCl_2[NPCl(OCH{=}CH_2)]$ is a useful precursor in polymerization reactions.

It has been shown recently that hexahalogenocyclotriphosphazenes $(NPX_2)_3$ (X = F or Cl) undergo reactions with $Li[OC(R){=}CH_2]$ to yield the vinyloxy derivatives $N_3P_3X_{6-n}[OC(R){=}CH_2]_n$ (X = F, R = H, n = 1—5;[1,2] X = Cl, R = H, n = 1—6;[3] X = Cl, R = Me, n = 1[4]). Some of these derivatives are potential polymer precursors.[5,6] We have investigated the reaction of the lithium enolate of acetaldehyde, Li(OCH=CH_2), with the cyclothiaphosphazenes $[NS(O)Ph]_{3-n}(NPCl_2)_n$ (n = 1 or 2). This study was carried out in order to (*i*) prepare monovinyloxy derivatives in high yields which could be used in polymerization studies, and (*ii*) isolate the possible isomers formed at various substitution stages.

Results and Discussion

The reaction between $[NS(O)Ph](NPCl_2)_2$ (**1**) and Li(OCH=CH_2) leads to substitution at phosphorus, the degree of substitution depending on the molar ratios used. The ^{13}C n.m.r. spectrum† of the monosubstituted derivative (**2**) is consistent with a vinyloxy rather than an aldehyde group.[7] This means that the vinyloxy group (enolate anion) of Li(OCH=CH_2) attacks the phosphorus through the oxygen atom [equation (1)], as was found for similar reactions with $(NPX_2)_3$ (X = F or Cl).[1,2]

$$[NS(O)Ph](NPCl_2)_2 \xrightarrow{Li(OC_2H_3)} [NS(O)Ph]N_2P_2Cl_{4-n}(OCH{=}CH_2)_n \quad (1)$$
$$n = 1\text{—}4$$

Only one of the two possible isomers of $[NS(O)Ph]NPCl_2[NPCl(OCH{=}CH_2)]$ (**2**) could be detected in the various reaction mixtures. Interaction between Li(OCH=CH_2) and the sulphur-bonded oxygen, similar to that reported for nucleophilic additions to carbonyl compounds,[8] combined with steric constraints may lead to the stereospecific formation of only one isomer, most likely possessing the *trans* structure[9] (see Figure).

Compound (**2**) appears to be very reactive in further substitution reactions. Even when using a 1:1 molar ratio of the reactants a disubstituted product (**3**) is formed in appreciable amounts. Since this isomer shows only one signal (δ_P = 15.7 p.p.m.) in the ^{31}P n.m.r. spectrum, it should have the 1α,3β,5β structure (see ref.9 for nomenclature). The alternative 1α,3α,5β structure can be eliminated as it is expected to give an AB-type pattern in the same region. Raising the amount of the enolate present to a 1.5 molar ratio the ^{31}P n.m.r. spectrum of the crude reaction mixture shows, in addition to the resonance lines of (**2**) and (**3**), a low-intensity AX pattern [δ_P = 25.2, −2.0 p.p.m.; $^2J(PP)$ = 79.4 Hz], which is tentatively ascribed to the geminal isomer $[NS(O)Ph]NPCl_2[NP(OCH{=}CH_2)_2]$ (**4**) {compare $(NPCl_2)_2[NP(OCH{=}CH_2)_2]$: δ_P = 24.5, −0.6 p.p.m.; $^2J(PP)$ = 69.0 Hz[3]}. However, a non-geminal pathway is preferred for the second substitution step as the relative yield of (**4**) is small (5—10% based on n.m.r. data).

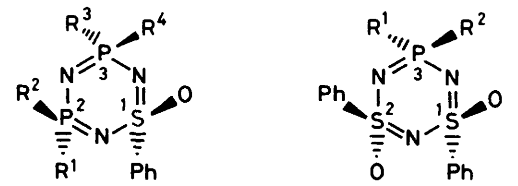

Figure. Compounds $[NS(O)Ph](NPR^1R^2)(NPR^3R^4)$ and $[NS(O)Ph]_2NPR^1R^2$. For (**2**): R^1 = Cl, R^2 = OCH=CH_2, R^3 = R^4 = Cl

Compound (**3**) reacts easily to give $[NS(O)Ph][NPCl(OCH{=}CH_2)][NP(OCH{=}CH_2)_2]$ (**5**); the assignment of a *trans* structure follows from the 1α,3β,5β structure of (**3**). Compound (**4**) is, in principle, capable of forming *cis*-$[NS(O)Ph][NPCl(OCH{=}CH_2)][NP(OCH{=}CH_2)_2]$ (**6**). Careful analyses of ^{31}P n.m.r. spectra of reaction mixtures with stoicheiometry 1:2 or 1:2.5 revealed a low-intensity AX pattern [δ_P = 18.5, 4.6 p.p.m.; $^2J(PP)$ = 86.5 Hz], which might be related to the presence of (**6**). Efforts to isolate compound (**6**) were unsuccessful because of its low concentration. Using an excess of Li(OCH=CH_2), $[NS(O)Ph][NP(OCH{=}CH_2)_2]_2$ (**7**) is the major derivative formed, showing the expected singlet in its ^{31}P n.m.r. spectrum. As observed for corresponding amino derivatives[10] the δ_P values of equally substituted phosphorus atoms increase with an increasing degree of substitution (Table 1).

The reaction of Li(OCH=CH_2) with *trans*-$[NS(O)Ph]_2NPCl_2$ (**8**) (see Figure, R^1 = R^2 = Cl) takes place smoothly and the mono [(**9**)] and bis [(**10**)] derivatives can be isolated in reasonable yields. The monovinyloxy derivatives (**2**) and (**9**) can easily form derivatives using other nucleophiles and leaving the vinyloxy group intact. The synthesis of $[NS(O)Ph][NP(az)_2][NP(az)(OCH{=}CH_2)]$ (**11**) (az = aziridin-1-yl) may serve as an example.

A pilot study on the reactivity of (**2**) in homo- and copolymerization reactions proved it to be a useful polymer precursor.[11]

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† For P–O–$C^1{=}C^2$; $\delta_C(CDCl_3)$ 139.9 [C^1, d, $^2J(CP)$ 8.9 Hz], 104.7 [C^2, d, $^3J(CP)$ 11.8 Hz].

Table 1. Analytical[a] and physical data[b] for compounds $[NS(O)Ph](NPR^1R^2)(NPR^3R^4)$ and $[NS(O)Ph]_2(NPR^1R^2)$

Compounds $[NS(O)Ph](NPR^1R^2)(NPR^3R^4)$						δ(P)[c]				Analysis (%)		
R^1	R^2	R^3	R^4		M.p. (θ/°C)	PCl_2	$PCl(OCH=CH_2)$	$P(OCH=CH_2)_2$	$^2J(PP)$[c]	C	H	N
Cl	Cl	Cl	Cl	**(1)**	91.5 92[d]	20.7[d]						
Cl	$OCH=CH_2$	Cl	Cl	**(2)**	Liquid	23.4	12.3		75.9	25.10 (25.40)	2.35 (2.15)	10.95 (11.10)
Cl	$OCH=CH_2$	Cl	$OCH=CH_2$	**(3)**	Liquid		15.7			30.90 (31.10)	2.95 (2.85)	10.70 (10.90)
$OCH=CH_2$	$OCH=CH_2$	Cl	Cl	**(4)**	Not isolated	25.2		−2.0	79.4			
$OCH=CH_2$	$OCH=CH_2$	Cl	$OCH=CH_2$	**(5)**	Liquid		18.3	1.6	88.6	36.55 (36.60)	3.60 (3.60)	10.60 (10.65)
$OCH=CH_2$	$OCH=CH_2$	$OCH=CH_2$	Cl	**(6)**	Not isolated		18.5	4.6	86.5			
$OCH=CH_2$	$OCH=CH_2$	$OCH=CH_2$	$OCH=CH_2$	**(7)**	27—29			4.3		41.65 (41.90)	4.30 (4.25)	10.45 (10.45)
Compounds $[NS(O)Ph]_2NPR^1R^2$												
Cl	Cl			**(8)**	124.5—126[d]	22.1[d]						
Cl	$OCH=CH_2$			**(9)**	Liquid		12.7			41.70 (41.85)	3.50 (3.25)	10.30 (10.45)
$OCH=CH_2$	$OCH=CH_2$			**(10)**	57—59			−2.9		46.85 (46.95)	4.00 (3.95)	10.20 (10.25)

[a] Required values in parentheses. [b] Apart from the Ph resonance the ^1H n.m.r. spectra of all vinyloxy derivatives show multiplets in the regions 4.5—5.3 and 6.2—6.8 p.p.m. [c] Chemical shifts (p.p.m.) positive to low field, coupling constants in Hz. [d] From ref. 13.

Table 2. Experimental data for reactions with $Li(OCH=CH_2)$

Starting compound (mmol)	$LiBu^n$ (mmol)	Products formed (%)[a]	Yield after purification (%)
(1), 2.5	2.5	**(1)**, 5; **(3)**, 30; **(2)**, 65	**(2)**, 50
(1), 2.5	3.7	**(2)**, 30; **(4)**, 10; **(3)**, 60	**(3)**, 40
(1), 2.5	5.0	**(3)**, 30; **(6)**, 10; **(4)**, 5; **(7)**, 5; **(5)**, 50	
(1), 2.5	6.2	**(3)**, 10; **(6)**, 5; **(5)**, 70; **(7)**, 15	**(5)**, 50
(1), 2.5	15.0	**(5)**, 10; **(7)** 90	**(7)**, 60
(8), 2.5	2.5	**(9)**, 100	**(9)**, 70
(8), 2.5	5.0	**(10)**, 90[b]	**(10)**, 60

[a] Based on ^{31}P n.m.r. spectra. [b] 10% Indefinable impurities.

Experimental

General.—All experiments were performed in an atmosphere of dry nitrogen. Solvents were purified and dried by conventional methods.[12] Compounds **(1)** and **(8)**, as well as $Li(OCH=CH_2)$ were prepared as described elsewhere.[1,13] Purification by h.p.l.c. was carried out using a Waters model 590 instrument, combined with a R401 RI detector. Separations were performed on Lichrosorb Si 60/10 columns (inside diameter 22 mm, length 30 cm) using n-hexane, containing 5% tetrahydrofuran, as eluant. ^1H N.m.r. spectra were recorded on a Bruker FT-90 instrument using $SiMe_4$ as internal standard. Phosphorus-31 and ^{13}C n.m.r. spectra were determined using a Nicolet NT200 instrument operating at 81.0 and 50.3 MHz, respectively. $(NPCl_2)_3$ in $CDCl_3$ ($\delta_P = 19.9$ p.p.m.) was used as an external reference for the ^{31}P spectra; $CDCl_3$ ($\delta_C = 76.9$ p.p.m.) as internal standard for ^{13}C spectra. Mass spectra were recorded as a routine purity check on an AEI MS9 mass spectrometer. Elemental analyses were carried out at the Microanalytical Department of the University of Groningen.

Reactions with $Li(OCH=CH_2)$.—The following is a typical reaction. Other reactions were carried out similarly, details are given in Table 2.

A solution of n-butyl-lithium (2.5 mmol) in hexane (1.6 cm^3) was added slowly to tetrahydrofuran (25 cm^3) at room temperature. This solution was stirred for 20 h at room temperature and then added to $[NS(O)Ph](NPCl_2)_2$ **(1)** (2.5 mmol), in tetrahydrofuran (25 cm^3) at 0 °C. The reaction mixture was stirred for 3 d at room temperature. The solvent was removed under reduced pressure, the residue dissolved in diethyl ether and filtered quickly through a silica column. The solvent was removed and the residue subjected to various spectroscopic measurements. The ^{31}P n.m.r. spectrum gave a clear idea about the composition of the mixture which, in this case, was found to contain **(1)**, **(2)**, and **(3)**. The mixture was separated by h.p.l.c. techniques; K' 1.88 **(1)**, 2.38 **(2)**, and 3.38 **(3)** for analytical column (inside diameter 4.6 mm, length 30 cm), Lichrosorb Si 60/7, eluant n-hexane containing 5% tetrahydrofuran.

Preparation of **(11)**.—To a stirred solution of **(2)** (1.0 mmol) in diethyl ether (25 cm^3), cooled at −80 °C, a solution of aziridine (16.0 mmol) in diethyl ether (25 cm^3) was added slowly. After warming to room temperature and stirring overnight the reaction mixture was refluxed during 6 h and then evaporated *in vacuo*. The residue was extracted three times with diethyl ether (50 cm^3). After evaporation of the combined extracts the crude product was recrystallized from diethyl ether yielding white *crystals* of **(11)** (0.27 g, 0.68 mmol, 68%), m.p. 115—118 °C (Found: C, 42.50; H, 5.25; N, 20.80. $C_{14}H_{20}N_6O_2P_2S$ requires C, 42.20; H, 5.05; N, 21.10%); $\delta_H(CDCl_3)$ 7.4—7.9 (5 H, m, C_6H_5), 6.3—6.7 (1 H, m, CH), 4.4—4.9 [2 H, m, CH_2 (vinyloxy)], 2.20 [8 H, d, $^3J(PH)$ 17.4 Hz, 4 CH_2], 1.98 [4 H, d, $^3J(PH)$ 16.9 Hz, 2 CH_2]; $\delta_P(CDCl_3)$ 34.7 $[P(az)_2]$, 22.1 $[P(az)(OCH=CH_2)]$, $^2J(PP)$ 50.4 Hz.

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