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in the spectrum of the reaction mixture having reacted overnight (see above), are assigned to the N—CH₃ and the H—C=S signals of 9 \((R^1 = H)\), respectively\(^{11,12}\). This was confirmed when after an overnight reaction the \(^1H\)-NMR spectra of the solutions of 1b, 1c and 1d in \(N_2D_4/D_2O\) were measured. In the case of 1c and 1d in the low field region a peak is observed between \(\delta 7.03-7.09\) i.e. the HC= singlet in 9 \((R^1 = H)\) where in the case of 1b this low-field singlet is absent but a peak is observed in the high field region at \(\delta 1.87\) i.e. the CH₃ in 9 \((R^1 = CH_3)\)\(^{13}\).

The three pyrazoles \(8b, 8c\) and \(8d\) which were isolated from the analogous reaction of the pyrimidinium salts 1b, 1c and 1d, are all deuterated at position 4. It was observed further that the 3,5-dimethyl-4-D-pyrazole \((8c)\) also contains deuterium in the methyl group as proved by the presence of peaks at \(m/e = M, M+1, M+2, M+3, M+4\) and \(M+5\) in the mass spectrum. Apparently, in the open-chain compounds 3, 4 and 5 the methyl group participates in the tautomerism since the alternative possibility – a H/D exchange in the methyl group of 3,5-dimethyl-4-D-pyrazole – does not take place under these mild conditions.

**Experimental part**

The \(^1H\)-NMR spectra were recorded on a Jeol JNM-C60 H spectrometer, using TMS \((\delta = 0)\) as internal standard. In the case of adduct measurements the apparatus was equipped with a JES-VT-3 variable temperature controller. Measurements of D contents were carried out on an AEI-MS 902 mass spectrometer.

**Preparation of the starting materials**

1-Methylpyrimidinium iodide \((1a)\), 1,2-dimethylpyrimidinium iodide\(^4\) \((1b)\), 1,4,6-trimethylpyrimidinium iodide\(^5\) \((1c)\) and 4-phenyl-1-methylpyrimidinium iodide\(^4\) \((1d)\) were prepared as described in the literature.

General procedure for measuring the \(^1H\)-NMR spectra in \(N_2D_4/D_2O\)

To 50 mg of the quaternized compound 1 being cooled at \(-30\)°, about 0.5 ml of precooled \((-30\)°) deuterated hydrazine hydrate (Merck, 80\% \(N_2D_4/D_2O\), deuteration ratio >99\%) was added. A yellow-orange coloured solution was obtained. TMS was added as internal standard. A sample of this solution was introduced in a \(^1H\)-NMR tube being cooled at \(-30\)°. The measurements started 10–15 min after addition.

The pyrazoles \(8a\)–\(d\) being obtained in the hydrazinolysis were isolated as described previously\(^3\).

**Acknowledgement**

One of the authors (M. S. Brouwer) wishes to thank the management of Philips Duphar B.V., Weesp, The Netherlands, for giving him the opportunity to carry out this work at the Laboratory of Organic Chemistry, Agricultural University, Wageningen, The Netherlands. We are indebted to K. A. L. Landheer for measuring the mass spectra.

\(^{12}\) It cannot be excluded that \(9\) undergoes hydrazinolysis in the presence of hydrazine leading to a replacement of the N(CH₃)₂ group. See: The Chemistry of the Carbon-Nitrogen double bond (1970) p. 81, 82, Ed. S. Patai. However, it does not change the assignments.

\(^{13}\) Compare Sadler system 5390 M: \((CH_3)_2N—CH=N—C_6H_4—pCl\); \(N—CH_3\) \(\delta 2.95\) and \(-CH=\) \(\delta 7.35\). See also 8325 M: \((CH_3)_2N—C(CH_3)=N—C_6H_4pCl\); \(N—CH_3\) \(\delta 3.00\) and \(—C(CH_3)=\) \(\delta 1.78\).


**Poly(iminomethylene), \(71\): Synthesis of diphenylphosphine-substituted poly[[1-phenylethyl]iminomethylene]**

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**Abstract.** Polymer-anchored phosphine functions were obtained in two ways: by diphenylphosphinolation of poly[[1-(4-bromophenylethyl)iminomethylene] and by polymerization of 1-[4(diphenylphosphino)phenyl]-1-isocyanoothane. The synthesis of the monomers and polymers is described.

**Introduction**

Many efforts have been made at anchoring homogeneous catalysts on insoluble supports. For this purpose materials like silica\(^2\) and polystyrene\(^3,4\) have frequently been used. This immobilization of a catalyst sometimes diminishes side-reactions\(^5\) and extends its lifetime. The anchoring of homogeneous catalysts on the usual types of polymeric supports suffers from a number of disadvantages. In most cases the secondary structure of the polymers and the surroundings of the catalytic centres are unknown. Often, the accessibility of the complexes is reduced, giving rise to lower activities\(^6\). The degree of introduction of phosphine groups, often used as interfaces between polymer and metal ion, appears to be low: 1 per 3–20 polymer side chains\(^7,8\). Moreover, the polymers usually contain some
Results and discussion

Millich has described the synthesis of 1-phenylethyl isocyanate and its polymerization by means of an acid-coated glass catalyst. We have synthesized 1-(4-bromophenyl)ethyl isocyanide, (3), in an analogous way starting from cyanide and its polymerization by means of an acid-coated series. The second type was synthesized by polymerization of a triphenylphosphine containing isocyanide. Applications of these polymers in catalysis will be described in subsequent papers of this series.

Scheme 1

accomplished by nickel chloride. The intrinsic viscosity of the polymer obtained, (4), was 0.31 dl/g. If we use the values of the Mark-Houwink constants determined for poly[(1-phenylethyl)iminomethylene] to estimate the molecular weight, a value of 40,000 is calculated.

The introduction of diphenylphosphine functions into polymer 4 was realized through lithiation with butyllithium and subsequent coupling with chlorodiphenylphosphine. The effect of the reaction conditions on the degree of exchange of bromine in 4 was determined from the elemental analysis (Table 1). The highest degree of functionalization, 50%, was obtained in 5b. This value is appreciably higher than most of the values reported for polystyrene resins. An explanation for this difference could be the better accessibility of the side groups in poly(iminomethylene).

Table 1 Lithiation of polymer 4 and coupling with chlorodiphenylphosphine.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymer composition</th>
<th>% Lithiation</th>
<th>% Coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>m: 0.62, n: 0.21, o: 0.17</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>5b</td>
<td>m: 0.40, n: 0.11, o: 0.49</td>
<td>90</td>
<td>55</td>
</tr>
</tbody>
</table>

a Reaction conditions 5a: 1.3 eq. BuLi, reaction time 2 h; 3.2 eq. Ph2PCl, reaction time 4 h; 5b: 2.1 eq. BuLi, reaction time 3 h; 7.2 eq. Ph2PCl, reaction time 96 h.

b m, n and o are the fractions of unsubstituted, bromine substituted and phoshine substituted phenyl groups, respectively.

Just like functionalized polystyrene resins, polymer 5 suffers from two disadvantages: the distribution of phosphorus over the polymer chain is unknown and the presence of bromine can affect the behaviour of the support, e.g. by quaternization of phosphine with a possibility of cross-linking. Therefore, we decided to synthesize also a poly(iminomethylene) with a phosphine function in each repeating unit (Scheme 2).

Scheme 2

Protection of the carbonyl function in 4-bromocetophenone, 1, by 1,2-ethanediol gave the acetal 6. Its product of lithiation can be used as a synthon for coupling with many types of reagent. Reaction of this synthon with chlorodiphenylphosphine gave the substituted triphenylphosphine 7. This compound was hydrolyzed to give 8 which was directly converted to N-formyl[1-[4-(diphenylphosphino)-phen]ethyl]amine, 9, via a Leuckart synthesis. Initial attempts to synthesize 9 through reaction of the Grignard or lithium derivative of 2 with chlorodiphenylphosphine failed. The isocyanide 10 was obtained in a yield of 75-85% by dehydration of 9 using either phosphoryl chloride or perchloromethyl formate, both in combination with triethylamine. Direct synthesis of 10 from isocyanide 3 by reaction with butylthiolium and chlorodiphenylphosphine gave unsatisfactory results.

The pale-yellow crystals of 10 were moderately soluble in ethanol and diethyl ether, and soluble in tetrahydrofuran, acetone, chloroform and dichloromethane. In chlorinated hydrocarbons slow decomposition was observed. In the infrared spectrum of 10 strong absorptions were visible at 2142 and 1430 cm⁻¹ indicative of the isocyanide and phenylphosphine functions. The structures of 10 and its precursors 8 and 9 were supported by elemental analysis, H, 13C, 31P-NMR and mass spectroscopy.

The isocyanide 10 was readily polymerized by treatment with nickel chloride. After isolation and fractionation, polymer 11 was obtained as a light yellow powder. The polymer was soluble in tetrahydrofuran, chloroform, benzene and toluene, and insoluble in the lower alcohols. The intrinsic viscosity of 11 was dependent on the amount of catalyst used: 5 mol % nickel chloride gave a polymer with [η] = 0.02 dl/g. Lowering the amount of catalyst to 0.5 mol % increased this value to [η] = 0.04 dl/g. Applying the Mark-Houwink equation as determined for poly(1-phenylethyliminomethylene), one calculates a molecular

weight in the range of 5,000–10,000. Usually, a molecular weight of 40,000–50,000 is found after polymerization of other isocyanides under these conditions. The lower values found for I1 might result from steric hindrance of polymerization by the bulky triphenylphosphine group.

Experimental part

Proton NMR spectra were obtained on Varian EM 360 and EM 390 spectrometers. The 13C- and 31P-spectra were recorded on a Varian CFT 20 and a Bruker WH 90 spectrometer, respectively. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Organic Chemistry TNO under supervision of W. J. Buis. NMR chemical shifts, δ, are given in ppm downfield from internal tetramethylsilane, unless otherwise stated. Abbreviations used are: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and dist = distorted. All solvents and reagents were dried and distilled under a nitrogen atmosphere. Chlorodiphenylphosphine and butyllithium (1.5 mol/1 in hexane) were purchased from Aldrich. All phosphorus-containing compounds were handled under rigorous exclusion of oxygen.

4-Bromoacetophenone (1) was synthesized in 82% yield in accordance with the literature. 1H-NMR (CDCl3): δ 2.50 (s, 3H, CH3), 7.50 and 7.75 (2 × d, 4H, arom.), 7.45 (2 × d, 4H, arom.), 8.10 (s, 1H, CHO).

N-Formyl-4-(4-bromomethyl)ethylenimine (2) was obtained from 1 and ammonium formate. Yield 82%: b.p. 156–160° (0.6 mm); 1H-NMR (CDCl3): δ 1.40 (d, 3H, CH3), 5.05 (m, 1H, CH), 7.15 and 7.45 (2 × d, 4H, arom.), 8.10 (s, 1H, CHO).

1-(4-Bromomethyl)ethyl isocyanide (3). An amount of 30 g (0.13 mol) of 2 in 220 ml of dichloromethane and 88 ml of triethylamine was treated with 13.5 ml (0.15 mol) of phosphor chloride as described by Ugi and Millich for a similar compound. After work up and distillation in vacuo, 23 g (83%) of 3 were obtained; b.p. 95–98° (0.9 mm); IR (neat): 2140 cm⁻¹; 1H-NMR (CDCl3): δ 1.60 (d, 3H, CH3), 4.70 (q, 1H, CH), 7.10 and 7.40 (2 × d, 4H, arom.).

Poly[[1-(4-bromomethyl)ethyl]iminomethylene] (4). A mixture of 4 g (20 mmol) of 3 and 7 mg (0.03 mmol) of nickel chloride hexahydrate was kept at 5°C for one month. The resulting solid was dissolved in benzene and poured into an excess of ether. A light-brown solid was obtained which was repeatedly extracted with ethanol. The residue was dissolved in tetrahydrofuran and added drop by drop to a hundredfold excess of ether. Collecting the solid and drying in vacuo afforded 3.2 g of creamish brown 5b. The calculated composition of 5b is given in Table I. It was based on: C 67.38, H 6.22, Br 9.54, P 2.90.

Acetal of 4-bromoacetophenone (6). This acetal was synthesized from 4-bromoacetophenone, 1, in a way similar to that described by Eliel. In 500 ml of benzene or toluene 199 g (1 mol) of 1, 68 g (1.2 mol) of 1,2-ethanediol and 0.01 g of 4-toluenesulfonic acid was added during 30 minutes. The white precipitate disappeared when 7 is recrystallized from ethanol, part of the acetal function is hydrolysed. 1H-NMR (CD3COCD3): δ 7.62, 7.75, 7.84, 7.90 (2 × m, 4H, arom.), 8.00 (s, 1H, CHO).

Polymer 5a was obtained in a similar way from 0.5 g (2.3 mmol) of 4, 3.1 mmol of butyllithium and 7.25 mmol of chlorodiphenylphosphine. The reaction time for lithiation was two hours and for coupling with chlorodiphenylphosphine four hours. The calculated composition of 5a is given in Table I. It was based on: C 67.38, H 6.22, Br 9.54, P 2.90.

Table 1 13C chemical shifts and 13C–31P coupling constants of compounds 8, 9 and 10.

<table>
<thead>
<tr>
<th>Compound</th>
<th>13C chemical shifts</th>
<th>31P chemical shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>26.56</td>
<td>194.31</td>
</tr>
<tr>
<td></td>
<td>136.78</td>
<td>127.95</td>
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<tr>
<td></td>
<td>2J = 7.1</td>
<td>2J = 13.22</td>
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<tr>
<td>9</td>
<td>2J = 13.44</td>
<td>144.36</td>
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<tr>
<td></td>
<td>1J = 10.7</td>
<td>1C = 135.90</td>
</tr>
<tr>
<td></td>
<td>2J = 13.44</td>
<td>1C = 128.98</td>
</tr>
<tr>
<td>10</td>
<td>2J = 13.44</td>
<td>1C = 128.48</td>
</tr>
<tr>
<td></td>
<td>2J = 13.44</td>
<td>1C = 128.29</td>
</tr>
<tr>
<td></td>
<td>2J = 13.44</td>
<td>1C = 128.29</td>
</tr>
</tbody>
</table>

The chemical shifts are in ppm relative to tetramethylsilane; the 13C–31P coupling constants are in Hz.

The numbering of the carbon atoms is as follows:

(a) The 13C resonance of the C=O carbon is at 160.82.
(b) The 13C resonance of the isocyanide carbon was not observed.
2 ml of water. This mixture was shaken for 30 minutes, water was added and the solution was decanted and the content crystallized. Crystallization from ethanol afforded 0.38 g (80%) of 8; m.p. 106-108°; IR (KBr): 3400-2700 (hydroxy), 3000-2500 (aromatic), 2850-2900 (aliphatic), 1740 (C=O); "H-NMR (CDCl3): 3.8 (s, 3H, CH3), 7.30 and 7.40 (br, 14H, arom.). For the 13C-NMR spectrum see Table II.

N-Formyl[l-4-(diphenylphosphino)phenyl]ethylamine (9). This formamide was synthesized from 7 via a Leuckart synthesis. To 34.8 g (0.10 mol) of 7 were added 100 ml of formamide, 25 ml of formic acid and 2 ml of water. This mixture was kept overnight; the solution was heated to 180-190° and at regular intervals 20 ml of portions of formic acid were added and water was distilled off. In this way 10 portions were added during 25 hours of heating. This procedure was followed by addition of two portions of 25 ml of toluene at a temperature of 200°. After cooling, the solution was poured into 400 ml of water/diethyl ether/THF (1:1:1 v/v). The aqueous layer was extracted 4 times with 150 ml ether/THF (1:1 v/v); the combined organic layers were washed 3 times with 1% Na2CO3 solution and 3 times with water. The latter aqueous layers were extracted once with ether. The combined ether/THF solutions were dried over MgSO4. After filtration the solution was concentrated in vacuo (50°, 0.1 mm) to give 29 g (85%) of a white solid, 9, which was used without further purification for the synthesis of the isocyanide 10.

An amount of 13 g of 9 was recrystallized from ethanol. After drying in vacuo (0.1 mm) over P2O5, 9.1 g of white crystals resulted; m.p. 123.5-124.5°; (C21H18NOP)0.3; calc. C 79.98, H 5.75, N 4.26, P 9.82; found C 79.53, H 6.12, N 4.47, P 9.70, no oxygen or nitrogen due to the presence of triphenylphosphine oxide moieties as was shown in separate experiments.

[1-4-(Diphenylphosphino)phenyl]-1-isocyanooctane (10). The isocyanide 10 was synthesized from 9 in two ways. The first method was analogous to the synthesis of 3, yield 70%. The second method used perchloromethyl formate to 16.6 g (0.05 mol) of 9 and 10.7 g (0.01 mol) of triethylamine in 50 ml of dichloromethane were added 4.85 g (0.025 mol) of perchloromethyl formate in 30 ml of dichloromethane at a temperature of -10° during one hour. Stirring was continued for one hour while the temperature was allowed to rise to 20°. The solution was rapidly washed with 50 ml of cold water and with 75 ml of a 7.5% NaHCO3 solution. The dichloromethane solution was rapidly concentrated in vacuo (20°, 10 mm) and the residue dissolved in dry THF. This solution was dried over molsieve 4A, filtered and concentrated in vacuo (20°, 1 mm). The yield was 12.9 g (82%) of a yellow-brown solid. The solid was crystallized from ethanol (highest temp. 35°). The light yellow crystals were dried in vacuo (20°, 0.03 mm); m.p. 84.0-85.3°. According to elemental analysis the crystals contained ethanol: (C12H14N2P) (C6H6O)0.3 (CH3OH)0.3 (329.2); calc. C 78.80, H 6.06, N 4.26, P 9.41, O 1.46; found C 78.32, H 6.10, N 4.44, P 9.72, O 1.44; IR (KBr): 2142.0 ± 0.5 (NC, CO calibration), 2000-1700 (mono- and disubst. arom.), 1580 (arom.), 1480 and 1390 (CH3), 1430 (P-Ph, arom.), 1360, 1330, 1300, 1260, 1235, 1190 (C=0), 1165, 1150, 1120 (arom.), 750 and 700 (monosubst. arom.) cm-1; "H-NMR (CDCl3): δ 2.55 (6, 3H, CH3), 7.30 and 7.40 (br, 14H, arom.). For the 13C-NMR spectrum see Table II.

Acknowledgement

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