in the spectrum of the reaction mixture having reacted overnight (see above), are assigned to the N—CH₃ and the H—C= signals of 9 (R¹ = H), respectively. This was confirmed when after an overnight reaction the ¹H-NMR spectra of the solutions of 1b, 1c and 1d in N₂D₄:D₂O were measured. In the case of 1c and 1d in the low field region a peak is observed between δ 7.03–7.09 i.e. the HC= in 9 (R¹ = H) where in the case of 1b this low-field singlet is absent but a peak is observed in the high field region at δ 1.87 i.e. the CH₃ in 9 (R¹ = CH₃)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 (δ = 0) as internal standard. A sample of this solution was introduced in a JES-VT-3 variable temperature controller. Measurements of D contents were measured. In the case of adduct 4b, 4c and 4d, respectively11,12. This was about 0.5 ml of precooled (−30°C) deuterated hydrazine hydrate (Merck, 80% N₂D₄:D₂O, 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°C. The measurements started 10–15 min after addition.

The pyrazoles 8a–d being obtained in the hydrazinolysis were isolated as described previously³.

Acknowledgement

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A. J. Naaktgborn, R. J. M. Nolte and W. Drenth

Department of Organic Chemistry of the University, Croesestraat 79, Utrecht, The Netherlands (Received August 31st, 1977)

Abstract. Polymer-anchored phosphine functions were obtained in two ways: by diphenylphosphination 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 silica² and polystyrene—³,⁴ have frequently been used. This immobilization of a catalyst sometimes diminishes side-reactions⁵ 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 complex is reduced, giving rise to lower activities⁶. 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 chains⁷,⁸. Moreover, the polymers usually contain some 1-phenyl-1-methylpyrimidinium iodide¹⁴ (1d) were prepared as described in the literature.

General procedure for measuring the ¹H-NMR spectra in N₂D₄:D₂O

To 50 mg of the quaternized compound 1 being cooled at −30°C, about 0.5 ml of precooled (−30°C) deuterated hydrazine hydrate (Merck, 80% N₂D₄:D₂O, 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°C. The measurements started 10–15 min after addition.

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Results and discussion

Millich has described the synthesis of 1-phenylethyl isocyanide and its polymerization by means of an acid-coated glass catalyst\(^1\). We have synthesized 1-(4-bromophenyl)-ethyl isocyanide, (3), in an analogous way starting from 4-bromoacetophenone (Scheme 1). Polymerization of 3 was accomplished by nickel chloride\(^13\). 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-phenethyliminomethylene]\(^14\) 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 I). The highest degree of functionalization, 50%, was obtained in 5b. This value is appreciably higher than most of the values reported for polystyrene resins\(^7,8\). An explanation for this difference could be the better accessibility of the side groups in polyiminomethylene.

Table I Liithiation of polymer 4 and coupling with chlorodiphenylphosphine.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymer composition(^a)</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. Ph\(_2\)PCl, reaction time 4 h; 4b: 2.1 eq. BuLi, reaction time 3 h; 7.2 eq. Ph\(_2\)PCl, reaction time 96 h.

\(^b\) m, n and o are the fractions of unsubstituted, bromine substituted and phosphine 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\(^1\). Therefore, we decided to synthesize also a polyiminomethylene\(^a\) with a phosphine function in each repeating unit (Scheme 2).

Scheme 2

Protection of the carbonyl function in 4-bromoacetophenone, 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)phenyl]ethyl]amine, 9, via a Leuckart synthesis\(^15\). 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\(^1\) or perchloromethyl formate\(^1\), both in combination with triethylamine. Direct synthesis of 10 from isocyanide 3 by reaction with butylthiium 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, \(^1\)H-, \(^13\)C-, \(^31\)P-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 is 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 [\(\eta\)] = 0.02 dl/g. Lowering the amount of catalyst to 0.5 mol % increased this value to [\(\eta\)] = 0.04 dl/g. Applying the Mark-Houwink equation as determined for poly(1-phenethyliminomethylene), one calculates a molecular
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/l 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.1 1H-NMR (CCl4): δ 2.50 (s, 3H, CH3), 7.50 and 7.75 (2 x d, 4H, arom.).

N-Formyl-4-bromophenylmethanamine (2) was obtained from 1 and ammonium formate.2 Yield 82%: δ 1.56-160 (0.6 mm); 1H-NMR (CDCl3): δ 1.40 (d, 3H, CH3), 5.05 (m, 1H, CH), 7.15 and 7.45 (2 x d, 4H, arom.). 8.10 (s, 1H, CHO).

1-(4-Bromophenyl)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 phosphoryl chloride as described by Ugi and Millich.4 After work up and distillation in vacuo, 23 g (83%) of 3 were obtained; δ 95-98° (0.9 mm); IR (neat): 2140 cm⁻¹ (N=C); 1H-NMR (CDCl3): δ 1.60 (d, 3H, CH3), 4.70 (q, 1H, CH), 7.10 and 7.40 (2 x d, 4H, arom.).

Poly[[1-(4-bromophenyl)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° for one month. The resulting solid was dissolved in benzene and poured into a hundredfold excess of methanol/water (9:1, v/v). The precipitate was collected by filtration and dried over P2O5 at 50° (12 mm); yield 3.2 g (80%) of yellow-orange 4. As indicated by elemental analysis our sample of 4 contained some residual benzene: C 73.80, H 6.23, Br 3.68, P 6.61; IR (KBr): 2000-1700 (mono- and disubst. arom.), 1620 (N=C), 1435 (P—Ph), 825 (disubst. arom.); 730 and 690 (monosubst. arom., C=Br) cm⁻¹.

Polymer 5a was obtained in a similar way from 0.5 g (2.3 mmol) of 4, 3.1 mmol of butyllithium and 1.6 g (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.

Acetal of 4-bromoacetophenone (6). This acetal was synthesized from 4-bromoacetophenone, 1, in a way similar to that described by Eliel and Adams.18, 19 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-toluene sulfonic acid were dissolved and water was removed by azeotropic distillation for 30 h. After work up and drying over K2CO3, benzene was removed by distillation and the residue was distilled in vacuo; yield 75-85%; δ 88-90° (0.6 mm), or 134-136°C (28 mm); 1H-NMR (CCl4): δ 1.50 (s, 3H, CH3), 3.60 and 4.00 (2 x m, 4H, CH2—CH2), 7.30 (s, 4H, arom.).

Acetal of 1-(diphenylphosphino)acetophenone (7). To 57 g (0.25 mol) of 6 in 200 ml of dry ether was added 200 ml (0.3 mol) of butyllithium in hexane at a temperature of -5° during two hours. The solution was stirred for another two hours at 0-5°, during which time a white precipitate was formed. At a temperature of ~15°, 66 g (0.3 mol) of chlorodiphenylphosphine in 150 ml of dry ether were added during 30 minutes. The white precipitate disappeared and the solution became yellow. The reaction mixture was kept overnight at a temperature of 0-10°; 200 ml of satd. NH4Cl solution was added and the organic layer separated. The aqueous layer was extracted with ether, the combined ethereal layers were washed twice with small portions of water and dried over K2CO3; yield 74 g (85%) of 7. The product contained 4% of n-butyldiphenylphosphine. If HCl is used instead of NH4Cl during work up, or when 7 is recrystallized from ether, part of the acetal function is hydrolysed. 1H-NMR (CD3COCD3): δ 1.50 (s, 3H, CH3), 3.60 and 3.90 (2 x m, 4H, CH2—CH2), 7.4 (br, 14H, arom.).

4-(Diphenylphosphino)acetophenone (8). To a small portion of 7 (0.54 g) were added 0.5 ml of formic acid, 0.5 ml of chloroform and a solution of butyllithium in ether. A red-brown precipitate was formed. The mixture was stirred for three hours. Subsequently, 18 ml (0.10 mol) of chlorodiphenylphosphine were added and stirring was continued for four days at room temperature; during this time the precipitate dissolved. After addition of 200 ml of satd. NH4Cl solution, the organic layer was separated, washed and concentrated in vacuo. The resulting oil was dissolved in acetone 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 the elemental analysis: C 73.80, H 6.23, Br 3.68, P 6.61; IR (KBr): 2000-1700 (mono- and disubst. arom.), 1620 (N=C), 1435 (P—Ph), 825 (disubst. arom.). 730 and 690 (monosubst. arom., C=Br) cm⁻¹.

Table I

<table>
<thead>
<tr>
<th>Compound</th>
<th>13C Chemical shifts and 31P coupling constants of compounds 8, 9 and 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>127.95 (J1 = 7.1, J2 = 18.6)</td>
</tr>
<tr>
<td>C2</td>
<td>134.22 (J1 = 14.3, J2 = 10.7)</td>
</tr>
<tr>
<td>C3</td>
<td>144.36 (J1 = 19.8, J2 = 6.0)</td>
</tr>
<tr>
<td>C4</td>
<td>136.02 (J1 = 19.1, J2 = 6.9)</td>
</tr>
<tr>
<td>C5</td>
<td>135.90 (J1 = 19.6, J2 = 6.8)</td>
</tr>
<tr>
<td>C6</td>
<td>128.98 (J1 = 19.9, J2 = 6.9)</td>
</tr>
<tr>
<td>C7</td>
<td>128.48 (J1 = 19.9, J2 = 6.9)</td>
</tr>
</tbody>
</table>

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

b The numbering of the carbon atoms is as follows:

```
  1  2  3  4  5  6  7  8  9 10
  \_\_\_\_\_\_\_\_\_\_\_\_\_
```

c  The 13C resonance of the C=O carbon is at 160.82.

d  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. Crystallization from ethanol afforded 0.38 g (80%) of 8; m.p. 106-108°; IR (KBr): 2000-1700 (mono- and disubst. arom.), 1680 (C=O), 1580 (arom.), 1475 and 1390 (CH3), 1430 (P-Ph), 830 (1,4-disubst. arom.), 745 and 700 (monosubst. arom.) cm-1; 1H-NMR (CDCl3): δ 7.2-7.3 (br, 14H, arom.); 31P-NMR (CDCl3): < 5 4.76 ppm (relative to 85% H3PO4); the occurrence of the latter peak is neither shown in separate experiments. According to elemental analysis the crystals contained ethanol: (C21H20NOP) (C2H6O)0 3 (329.2); calc. C 79.98, H 5.75, N 4.44, P 9.75; found C 78.32, H 6.10, N 4.47, P 9.70, no oxygen or nickel could be detected (<0.2%); IR (KBr): 2000-1700 (mono- and disubst. arom.), 1617.5 ± 1.5 (ν(CH3)), 1580 (arom.), 1475 and 1396 (CH3), 1435 (P-Ph), 825 (1,4-disubst. arom.), 745 and 695 (monosubst. arom.) cm-1; 1H-NMR (CDCl3): δ 0.8-1.8 (Δν 30 Hz, br, 3H, CH3), 4.5-5.7 (very br, 1H, CH), 6.3-8.0 (Δν 22 Hz, br, 14H, arom.); 31P-NMR (CDCl3): δ 4.6 (Δν 50 Hz, br), 36 (Δν 75 Hz, br, intensity is 1/6 of main peak) ppm (relative to 85% H3PO4); the occurrence of the latter peak is neither the result of complexation of phosphate functions to nickel chloride nor due to the presence of triphenylphosphine oxide moieties as was shown in separate experiments.

Acknowledgement

This research was financially supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).