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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= signals of 9 (R¹ = H), respectively.¹¹¹² 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. 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-Methylpyrrolidinium iodide (1a), 1,2-dimethylpyrrolidinium iodide⁴ (1b), 1,4,6-trimethylpyrrolidinium iodide⁵ (1e) and 4-phenyl-1-methylpyrrolidinium 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.

The pyrazoles 8a-d being observed in the hydrazinolysis were isolated as described previously³.

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 Drs. C. A. Landheer for measuring the mass spectra.

Poly(iminomethylenes). 7¹. Synthesis of diphenylphosphine-substituted poly[(1-phenylethyl)iminomethylene]

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(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-isocyananoethene. 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 and polystyrene have frequently been used. This immobilization of a catalyst sometimes diminishes side-reactions 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, its reduced, giving rise to lower activities. 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. Moreover, the polymers usually contain some ²-

Residual chlorine or bromine. In earlier papers Millich\(^9\) and \(10^{10,11}\) showed that poly(iminomethylenes) have the configuration of a tightly coiled helix with side-chains protruding from a rodlike main chain. This property gives poly(iminomethylenes) major advantages for catalyst attachment: the catalytic centres are more accessible and the secondary structure is more uniform and better defined. The chirality of the main chain might be attractive for asymmetric catalysis.

In this paper we describe the synthesis of two types of triphenylphosphine containing poly(iminomethylenes). The first type was made by diphenylphosphination of poly[[1-(4-bromo-phenyl)ethyl]iminomethylene]. 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.

Results and discussion

Millich has described the synthesis of 1-phenylethyl isocyanide and its polymerization by means of an acid-coated glass catalyst\(^12\). We have synthesized \(1\)-(4-bromophenyl)-phenylethyliminomethylene, one calculates a molecular weight, a value of 40,000 is calculated. The introduction of diphenylphosphine functions into secondary structure is more uniform and better defined. The pale-yellow crystals of \(5\) were readily polymerized by treatment with nickel chloride. After isolation and fractionation, polymer \(11\) was obtained as a light yellow powder. The isocyanide \(10\) was obtained in a yield of 75-85% by dehydration of \(9\) using either phosphorol chloride\(^16\) or perchloromethyl formate\(^17\), both in combination with triethylamine. Direct synthesis of \(10\) from isocyanide \(3\) by reaction with butyllithium 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, \(\text{H}^1,^{13}\text{C},^{31}\text{P}-\text{NMR}\) and mass spectroscopy.

The isocyanide \(10\) was readily polymerized by treatment with nickel chloride. 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\(^3\). 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-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-diphenylphosphinopheno)-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 phosphorol chloride\(^16\) or perchloromethyl formate\(^17\), both in combination with triethylamine. Direct synthesis of \(10\) from isocyanide \(3\) by reaction with butyllithium and chlorodiphenylphosphine gave unsatisfactory results.

### Results and discussion

\(\text{Table I Lithiation of polymer 4 and coupling with chlorodiphosphine.}\)

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

\(\text{Table I Lithiation of polymer 4 and coupling with chlorodiphosphine.}\)

\(^a\) Reaction conditions \(5a\): 1.3 eq. BuLi, reaction time 2 h; 3.2 eq. Ph\(_2\)P\(_2\)Cl, reaction time 4 h; \(5b\): 2.1 eq. BuLi, reaction time 3 h; 7.2 eq. Ph\(_2\)P\(_2\)Cl, reaction time 96 h.

\(^b\) \(m, n\) and \(o\) are the fractions of unsubstituted, bromine substituted and phosphine substituted phenyl groups, respectively.
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 11 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/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.18 1H-NMR (CCl4): δ 2.50 (s, 3H, CH₃), 7.50 and 7.75 (2 x d, 4H, arom.).

N-Formyl[l-(4-bromophenyl)ethyl]amine (2) was obtained from 1 and ammonium formate.19 Yield 82%; δ 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 x d, 4H, arom.).

Poly[(1-[4-(bromophenyl)ethyl]imino)methylene] (4). A mixture of 4 g (20 mmol) of 3 and 7 mg (0.03 mmol) of nickel chloride hexa­hydrate was treated with 13.5 ml (0.15 mol) of phosphoryl chloride as anhydrous. A white precipitate was formed. The mixture was stirred for another two hours at 0-5°, during which time a white precipitate was formed. After addition of 200 ml of NH₄Cl solution, the organic layer was separated, washed and concentrated in vacuo.

A mixture of 1,2-ethanediol and 0.01 g of 4-toluenesulfonic acid was stirred for 48 h at 0-5° (under nitrogen). As indicated by elemental analysis our sample of 7 contained some residual benzene: [δ] = 0.31 dl/g (THF, 30.0°); IR (KBr): 1629 cm⁻¹ (C=O); 1H-NMR (CDCl₃): δ 0.9 and 1.3 (Av = 60 Hz, br, 6H, CH₃), 3.60 and 4.00 (2 x m, 4H, CH₂–CH₂), 7.30 (s, 4H, arom.).

Yield 75-85%; δ 88-90 (0.6 mm), or 134–136°C (28 mm); 13C-NMR (CDCl₃): δ 1.50 (s, 3H, CH₃), 3.60 and 4.00 (2 x m, 4H, CH₂–CH₂), 7.30 (s, 4H, arom.).

Acetal of 4-[(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 etheral layers were washed with water and dried over K₂CO₃. Yield 74 g (85%) of 7. The product contained 4% of β-butyldiphenylphosphine. If HCl is used instead of NH₄Cl during work up, or when 7 is recrystallized from ethanol, part of the acetal function is hydrolyzed. 1H-NMR (CDCl₃): δ 1.50 (s, 3H, CH₃), 3.60 and 3.90 (2 x m, 4H, CH₂–CH₂), 7.4 (br, 14H, arom.).

Acetal of 4-[(diphenylphosphino)acetophenone] (8). To a solution of 7 (0.54 g) were added 15 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.

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.

A. J. Naaktgeboren et al. / Synthesis of diphenylphosphino-substituted poly[(1-phenylethyl)iminomethylene]
N-Formyl[l-(4-(diphenylphosphino)phenoxy)ethyl]amine (9). This formamide was synthesized from 7 via a Leuckart synthesis[15]. 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 formic acid and 2 ml of water. This mixture was shaken for 30 minutes, water was distilled off. The latter aqueous layers were extracted once with ether. The combined ether/THF solutions were decanted and the solution concentrated. Crystallization from cold water and with 75 ml of a 7.5% NaHCO₃ solution. The di­solution was heated to 180-190° and at regular intervals 20 ml 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 a 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°; (C₂₁H₂₀NOP) (333.3); calc. C 79.98, H 5.75, N 4.44, P 9.82; found C 79.53, H 5.75, N 4.47, P 9.70, no oxygen or nickel chloride hexahydrate. The solution was stirred for four days at room temperature and the resulting suspension centrifuged; after decantation of the supernatant liquid the solid was twice suspended in methanol and isolated by centrifuga­tion. Drying in vacuo (30°, 0.01 mm) afforded 1.65 g (70%) of polymer 11 as a light yellow powder. It was dissolved in 10 ml of THF, fractionated over a deactivated silica column and eluted with THF/ethanol (10 : 1, v/v); yield 1.60 g. The first fraction (1.30 g) was dissolved in 10 ml of THF and added drop by drop to 200 ml of pure methanol, which was stirred rapidly. The resulting suspension was centrifuged and the supernatant liquor decanted. After drying in vacuo (35°, 0.005 mm) 1.19 g of 11 was collected; [α]D = 0.04 dl/g (toluene, 30.0°); (C₂₁H₂₀NOP) (315.3); calc. C 79.98, H 5.75, N 4.44, P 9.82; found C 79.53, H 5.62, 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 (N=C, H₂O vapour calibration), 1580 (arom.), 1475 and 1396 (CH₃), 1435 (P-Ph), 825 (1,4-disubt. arom.), 745 and 695 (monosubst. arom.) cm⁻¹; ¹3C-NMR ([CD₃]OD): δ 4.77 ppm (relative to 85% H₃PO₄); MS: M⁺ 315, M⁺-CH₃ 300, M⁺-CH₃-CH₃ 318, M⁺-HCO 304, M⁺-NHCHO 289, P(PhH) 185. For the ¹³C-NMR spectrum see Table II.

1-{[4-(Diphenylphosphino)phenoxy]-1-isocyanoethane (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[17]: 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 4Å, 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: (C₂₁H₂₀NOP) (C₂H₅OH) (329.2); calc. C 79.80, H 6.06, N 4.26, P 9.41; 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); 830 (1,4-disubst. arom.), 745 and 695 (monosubst. arom.) cm⁻¹; ¹H-NMR (CDCl₃): δ 2.55 (s, 3H, CH₃), 7.2-7.3 (br, 14H, arom.); 31P-NMR (CDCl₃): δ 4.15 (m, 3H, CH₃), 4.85 (q, 1H, CH), 7.2-7.3 (br, 14H, arom.); 85% H₃PO₄); MS: M⁺ 315, M⁺-CH₃ 300, M⁺-HCO 289, P(PhH) 185. For the ¹³C-NMR spectrum see Table II.

Poly[[l-{4-(diphenylphosphino)phenoxy}ethyliminomethylene] (11). By warming slightly an amount of 2.36 g (7.5 mmol) of crystallized 10 was dissolved in 8 ml of an ethanolic solution which contained 9 mg (0.5 mol %) of nickel chloride hexahydrate. The solution was stirred for four days at room temperature and the resulting suspension centrifuged; after decantation of the supernatant liquid the solid was twice suspended in methanol and isolated by centrifuga­tion. Drying in vacuo (30°, 0.01 mm) afforded 1.65 g (70%) of polymer 11 as a light yellow powder. It was dissolved in 10 ml of THF, fractionated over a deactivated silica column and eluted with THF/ethanol (10 : 1, v/v); yield 1.60 g. The first fraction (1.30 g) was dissolved in 10 ml of THF and added drop by drop to 200 ml of pure methanol, which was stirred rapidly. The resulting suspension was centrifuged and the supernatant liquor decanted. After drying in vacuo (35°, 0.005 mm) 1.19 g of 11 was collected; [α]D = 0.04 dl/g (toluene, 30.0°); (C₂₁H₂₀NOP) (315.3); calc. C 79.98, H 5.75, N 4.44, P 9.82; found C 79.53, H 5.62, 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 (N=C, H₂O vapour calibration), 1580 (arom.), 1475 and 1396 (CH₃), 1435 (P-Ph), 825 (1,4-disubt. 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).