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REGIO- AND STEREOSPECIFIC IODOCHLORINATION OF ALKENES AND ALKYNES WITH POLY{STYRENE-[4-VINYLPYRIDINIUM DICHLOROIODATE(I)]}

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Abstract - Poly{styrene-[4-vinylpyridinium dichloroiodate(I)]} can be used for regio- and stereospecific iodochlorination of different alkenes and phenylsubstituted alkynes. In all cases the reaction followed the Markownikov type of regioselectivity and the addition proceeded stereospecifically trans.

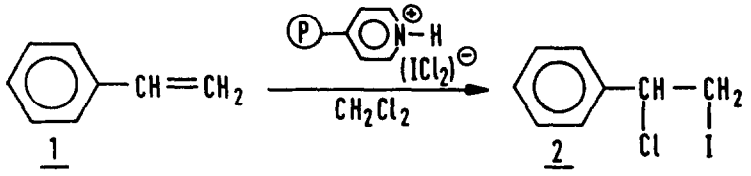
It is known that pyridine has broad application in organic synthesis, and in the last ten years poly(vinylpyridine) was found to be useful as an HCl acceptor[1], while bromine complexes of poly(vinylpyridine) and the copolymer of styrene and vinylpyridine were used as brominating agents for various types of organic compounds[2], poly(vinylpyridinium chlorochromate) as an oxidizing agent[3], poly(vinylpyridine borane) complex as a reducing agent[4], poly(vinylpyridine) as a matrix for protein immobilisation[5], and the poly(vinylpyridine)-copper complex as a catalyst for polymerization[6].

Recently, we have prepared a new polymeric reagent, crosslinked poly{styrene-[4-vinylpyridinium dichloroiodate (I)]} which can be used as a very efficient polymeric reagent for selective electrophilic iodination of activated benzene and naphthalene derivatives[7], some heterocyclic systems[7], as well as for α-iodination of ketones and corresponding enolacetates[8].

We now wish to report that poly{styrene-[4-vinylpyridinium dichloroiodate (I)]} can be used for regioselective and stereospecific iodochlorination of alkenes and alkynes. The great advantage of our polymer-supported reagent over the unsupported iodochloride lies in its inability to disproportionate, which leads to products of much higher purity. Vicinal iodochlorides, formed in the reactions with unsupported iodochloride, are contaminated with iodine, which demands several purification steps for products known for their instability and usually the isolation of pure products is not possible.

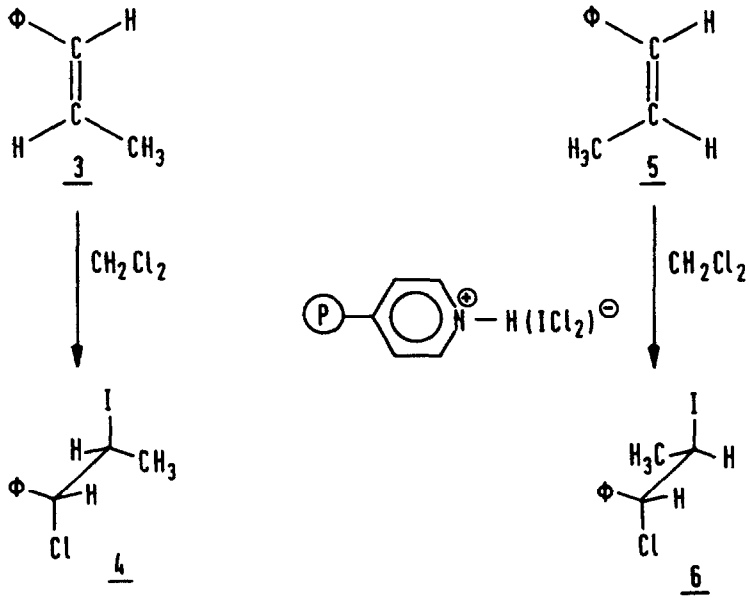
In a 20-h reaction of the polymeric reagent with styrene in methylene chloride solution at room temperature, the complete conversion of styrene to 1-chloro-1-phenyl-2-iodoethane(2)[9] (Scheme 1) as the only product was established. No regioisomer was formed, as determined by ^1H nmr spectroscopy of the crude reaction mixture. The same result was obtained when the reaction was carried out for two hours in refluxing methylene chloride.

SCHEME 1



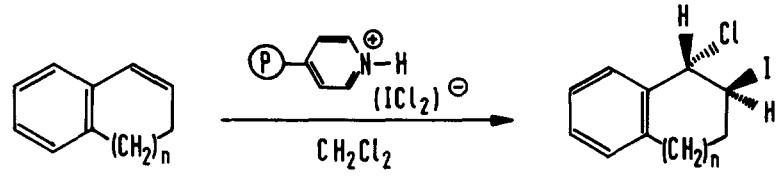
As the iodochlorination of styrene proceeded regioselectively, we chose both isomers of 1-phenylpropene to study the stereochemistry of the addition. Reactions in methylene chloride solution at room temperature in both cases followed the Markownikov type of regioselectivity and the addition proceeded stereospecifically trans (Scheme 2) and d,l-erythro-1-chloro-1-phenyl-2-iodopropane (4)[10] in the case of E isomer and d,l-threo-1-chloro-1-phenyl-2-iodopropane (6)[10] in

SCHEME 2



the case of Z-alkene was formed. The stereochemistry of the products was determined on the basis of their ^1H nmr spectra: the doublet signal at δ = 5.04 ppm with the coupling constant ^3J = 10.5 Hz corresponded to the hydrogen atom at C-1 in d,l-erythro isomer, while on the other hand the signal at δ = 5.05 ppm(d) with the coupling constant ^3J = 6 Hz in d,l-threo isomer was of significant importance for their characterization. Further, we studied the reaction with the cyclic analogue of 1-phenyl-1-propene: indene. Two hours reaction of 1 mmol of indene with 1 g of polymeric reagent in methylene chloride under reflux led to 36 % conversion, while complete conversion of the starting alkene was observed when the reaction was carried out at room temperature for 24-hours. On the basis of ^1H nmr data and by their comparison with the literature[11] we determined that the reaction also followed the Markownikov type of regioselectivity and proceeded stereospecifically trans, with the formation of trans-1-chloro-2-iodoindane(8)[11] (Scheme 3).

SCHEME 3



7 (n = 0)
9 (n = 1)

8 (n = 0)
10 (n = 1)

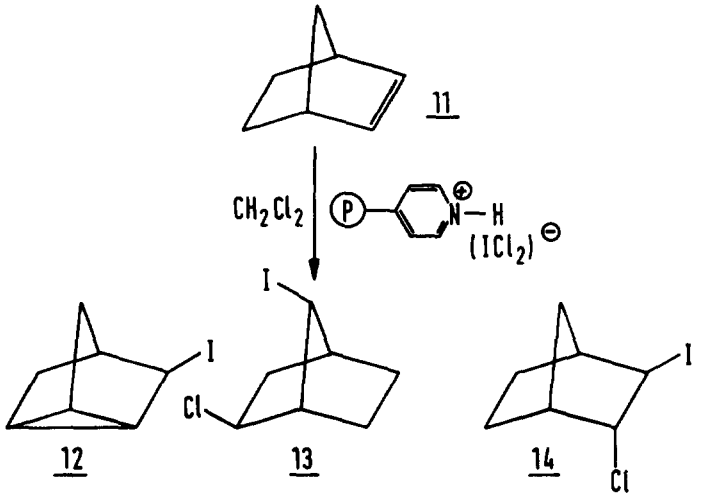
In order to determine the influence of the ring size on the regio- and stereochemistry of addition, we studied the reaction with 1,2-dihydronaphthalene. The reaction was carried out under the same reaction conditions as in the previous case and also only one product was obtained. Comparison of the nmr data of the product formed in the reaction with indene and those of the product obtained with 1,2-dihydronaphthalene (the coupling constant H_1, H_2 being 3 Hz in both cases is of significance) led us to the conclusion that trans-1-chloro-2-iodo-1,2,3,4--tetrahydronaphthalene(10) was formed (Scheme 3). Trans addition was also observed when the isomeric 1,4-dihydronaphthalene reacted and trans-2-chloro-3-iodo-1,2,3,4-tetrahydronaphthalene was obtained.

We also studied the reaction with norbornene which has often been used to differentiate the ionic or radical character of various reactions. It is known from the literature that the addition of iodochloride to norbornene in the presence of pyridine proceeds to the formation of three main

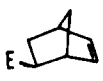
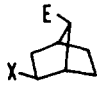
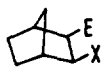
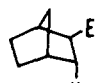
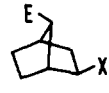
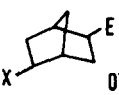
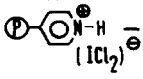
products[12]: iodonortricyclane(12), 2-exo-chloro-7-syn-iodonorbornane(13) and 2-endo-chloro-3--exo-iodonorbornane(14).

The reaction of norbornene with the polymeric reagent in methylene chloride at room temperature also resulted in the formation of three products. The distribution of the products showed that the course of the reaction is similar to that of norbornene with iodochloride in the presence of pyridine, except for the higher percentage of 2-exo-chloro-7-syn-iodonorbornane formed (Scheme 4).

SCHEME 4

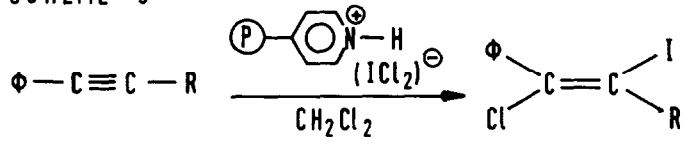


THE EFFECT OF THE REAGENT ON THE COURSE OF THE REACTION WITH NORBORNENE

	RELATIVE YIELDS							
EX								OTHERS
Cl_2	1	65	12	14		6		2
Br_2	1	52	27	1	4	12	5	—
ICl	1	12	40	1	35	5	2	7
		9	59	—	32	—	—	—

The regioselectivity and stereochemistry of iodochlorination of phenyl-substituted alkynes was also studied. In order to study the effect of the magnitude of the alkyl group on the regioselectivity and stereochemistry of the addition, the following substrates were chosen: phenylethyne, 1-phenylpropyne and 1-phenyl-3,3-dimethyl-1-butyne. 20-h reaction of 1 mmol of phenylethyne with 1 g of polymeric reagent at room temperature led to complete conversion of the starting acetylene with one product formation. The singlet signal at δ = 6.76 ppm in the ^{1}H nmr spectrum indicated (being in accord with the literature ones[13]) that E-1-chloro-1-phenyl-2-iodoethene (16) was formed. The same regioselectivity and stereochemistry of addition was observed in the reaction with 1-phenyl-1-propyne and the signal for the methyl group at δ = 3.16 ppm in the ^{1}H nmr spectrum is in accord with the literature[13]. No reaction with 1-phenyl-3,3-dimethyl-1-butyne was found, the ^{1}H nmr spectrum of the crude reaction mixture showing only signals corresponding to the starting acetylene. The steric interaction of the bulky t-butyl group bonded to the sp hybridized carbon atom probably prevented reaction (Scheme 5).

SCHEME 5



R = -H (15) 16

R = -CH_3 (17) 18

In conclusion, poly{styrene-[4-vinylpyridinium dichloroiodate(I)]} can be used for regio and stereospecific iodochlorination of alkenes and alkynes, and the products formed are isolated in pure form even in cases when their stability is low, since only a simple isolation procedure is needed (the polymer beads are just filtered off and the solvent evaporated in vacuo). The regio- and stereospecifity of the addition can be explained by the formation of a cyclic iodonium intermediate, followed by the attack of a chlorine anion from the opposite side.

EXPERIMENTAL

I.r. spectra were recorded using a Perkin-Elmer 727 B instrument, and ^{1}H nmr spectra on a JEOL JNM-PS-100 with Me_4Si as internal reference. Mass spectra were taken on a CEC-21-110 spectrometer. Tlc was carried out on Merck-PSC-Fertigplatten Kieselgel F 254. Melting points were determined on a Kofler apparatus and are uncorrected.

Styrene, E-1-phenyl-1-propene, indene, norbornene, phenylethyne, and 1-phenyl-1-propyne were commercially available and purified before use. Z-1-Phenyl-1-propene[14], 1,2-dihydronaphthalene[15], 1,4-dihydronaphthalene[15] and 1-phenyl-3,3-dimethyl-1-butyne[16] were prepared by known methods.

Preparation of Poly{Styrene-[4-Vinylpyridinium Dichloroiodate (I)]}

Thirty five grams of crosslinked poly(styrene-4-vinylpyridine)[17], containing 42-44% of pyridine rings was suspended in 150 ml of chloroform, cooled to 0°C and 30 g of 36% HCl was added. After stirring at 0°C for 30 minutes, 30 g of ICl was slowly added. The suspension was stirred at 0°C for another 60 minutes and at room temperature for 30 minutes. The polymer was filtered off, washed with methanol and chloroform, and after drying to a constant weight at room temperature, 70 g of polymeric reagent was obtained. Three hours of drying of 1 g of polymer at 100°C gave 0.93 g of polymeric reagent, containing 30.0% of iodine and 16.6% of chlorine (calculation for poly{styrene-[4-vinylpyridinium dichloroiodate (I)]} containing 43 % of pyridine rings: 29 % of iodine and 16.2 % of chlorine), which means that the polymeric reagent contained 2.2 mequiv of $(ICl_2)^-$ per gram of resin.

General Reaction Procedure

1 mmol of substrate was dissolved in 20 ml of methylene chloride and 1 g of poly{styrene-[4-vinylpyridinium dichloroiodate (I)]} was added. The reaction mixture was stirred or heated at a given temperature for a given time, the insoluble beads were filtered off, washed with 10 ml of CH_2Cl_2, the solvent evaporated in vacuo and the crude product purified.

Iodochlorination of Styrene

Reaction conditions: 25°C, 20 hours. The crude product was crystallized from ethanol and 180 mg (67%) of 1-chloro-1-phenyl-2-iodoethane(2) was obtained[9]; ^{1}H nmr ($CDCl_3$) δ = 3.66(2 H,m,H-2), 4.98(1 H,dd,J = 9 Hz, 6 Hz, H-1), 7.21 ppm (5 H,s, aromatic H's), M_p 41-42°C (lit. 46°C [9]).

Iodochlorination of E-1-Phenyl-1-Propene

Reaction conditions: 25°C, 5 hours. The crude reaction product was crystallized from methanol and 170 mg (61 %) of d,l-erythro-1-chloro-1-phenyl-2-iodopropane(4) was obtained; ^{1}H nmr ($CDCl_3$) δ = 2.19(3H,d,J = 6Hz,CH_3), 4.59(1H,m,H-2), 5.04(1H,d,J = 10.5 Hz,H-1), 7.32 ppm (5H,s,aromatic H's), mass spectra m/z (relative intensity): M+2 282(3), M^+ 280(9), 155(31), 154(10), 153(100), 127(10), 125(17), 118(42), 117(78), 116(10), 115(39), 91(54), 77(10). Found: m/z 279.9520, calcd for $C_9H_{10}ClI$: M, 279.9518, M_p 50-52°C (lit. 49.5-50.5°C [18]).

Iodochlorination of Z-1-Phenyl-1-Propene

Reaction conditions: 25°C, 5 hours. 173 mg(62 %) of oily d,l-threo-1-chloro-1-phenyl-2--iodopropane(6) (lit. $T_{0.3mmHg}$ = 92°C [18]) which decomposed on heating, was obtained; ^1H nmr(CCl_4) δ = 1.95(3H,d,J = 6Hz, CH_3), 4.62(1H,m,H-2), 5.05(1H,d,J = 6Hz,H-1), 7.36 ppm(5H,s,aromatic H's), mass spectra m/z (relative intensity) M+2 282(2), M^+ 280(6), 155(21), 153(92), 118(30), 117(100), 115(32), 91(43), 58(41). Found m/z 279.9520, calcd for $C_9H_{10}ClJ$: M, 279.9518.

Iodochlorination of Indene

Reaction conditions: 25°C, 24 hours. The crude reaction product was crystallized from methanol and 180 mg (65 %) of trans-1-chloro-2-iodoindane (8) was obtained[11]; ^1H nmr ($CDCl_3$) δ = 3.33 (1H,dd,J = 18Hz,3Hz,H-3), 3.84(1H,dd,J = 18Hz,6Hz,H-3), 4.68(1H,m,H-2), 5.52(1H,d,J = 3Hz, H-1), 7.15 ppm (4H,m,aromatic H's), M_p 47-49°C.

Iodochlorination of 1,2-Dihydronaphthalene

Reaction conditions: 25°C, 25 hours. The crude reaction product was crystallized from methanol and 180 mg (61 %) of trans-1-chloro-2-iodo-1,2,3,4-tetrahydronaphthalene(10) was obtained; ^1H nmr ($CDCl_3$) δ = 2.07 (2H,m,CH_2), 2.82(2H,m,CH_2), 4.77(1H,m,H-2), 5.4(1H,d,J = 3Hz,H-1), 7.06 ppm (4H,m,aromatic H's), mass spectra m/z (relative intensity): M+2 294(2), M^+ 292(7), 167(7), 165(25), 130(72), 129(100), 115(28), 102(8), 79(9), 64(11), 63(15), 51(29), 50(11). Found: m/z 291.9520, calcd for $C_{10}H_{10}ClJ$: M, 291.9518, M_p 49-51°C.

Iodochlorination of 1,4-Dihydronaphthalene

Reaction conditions: refluxing CH_2Cl_2, 2 hours. The crude reaction product was crystallized from methanol and 190 mg (65 %) of trans-2-chloro-3-iodo-1,2,3,4-tetrahydronaphthalene was obtained. ^1H nmr ($CDCl_3$) δ = 3.24(2H,m,CH_2), 3.84(2H,m,CH_2), 4.65(2H,m,H-2,H-3), 7.03 ppm (4H,m,aromatic H's), mass spectra m/z (relative intensity): M+2 294(5), M^+ 292(15), 167(9), 165(25), 130(25), 129(100), 128(34), 127(14), 115(11). Found: m/z 291.9520, calcd for $C_{10}H_{10}ClJ$: M, 291.9518, M_p 46-47°C.

Iodochlorination of Norbornene

Reaction conditions: 25°C, 5 hours. The crude reaction mixture was analysed by analytical GLC (SE 30 (10 %) on CHROMOSORB A/W 80/100 at 110°C) with the following retention times of products: 12(2.87), 13(11.82), and 14(6.49). All experiments were repeated several times with a maximum deviation of product distribution of ± 0.5 %. The products were isolated and characterized on the basis of a comparison of GLC retention times and spectroscopic data with authentic samples.

Iodochlorination of Phenylethyne

Reaction conditions: 25°C, 20 hours. The crude reaction product was purified by vacuum distillation (T_{5mmHg} = 112-113°C, lit. T_{5mmHg} = 112-113°C), and 230 mg (87 %) of E-1-phenyl-1-chloro-2-iodoethene(16)[13] was obtained; ^{1}H nmr (CCl_4) δ = 6.78 (1H,s,H-2), 7.5 ppm (5H,m,aromatic H's), mass spectra m/z (relative intensity): M+2 266(15), M^+ 264(48), 138(22), 127(19), 102(100), 101(21), 77(19), 76(19), 75(19). Found m/z 263.9200, calcd for C_8H_6ClJ: M, 263.9205.

Iodochlorination of 1-Phenyl-1-Propyne

Reaction conditions: 25°C, 20 hours. The crude reaction product was purified by vacuum distillation (T_{2mmHg} = 94-96°C, lit. T_{2mmHg} = 94-96°C) and 220 mg (80 %) of E-1-chloro-1-phenyl-2-iodo-1-propene(18)[13] was obtained. ^{1}H nmr (CCl_4) δ = 2.85(3H,s,CH_3), 7.42 ppm (5H,s,aromatic H's), mass spectra m/z (relative intensity): M+2 280(11), M^+ 278(34), 151(5), 127(9), 116(30), 115(100), 89(9), 63(12). Found m/z 277.9363, calcd for C_9H_8ClJ: M, 277.9361.

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