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M. Zupan[a]; B. šket[a]; Y. Johar[a]
[a] Department of Chemistry and "J. Stefan", Institute "E. Kardelj", University of Ljubljana, Ljubljana, Yugoslavia

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Synthesis and Properties of Cross-Linked 4-Vinylpyridine-Styrene-Halogen Complexes*

M. ZUPAN, B. ŠKET, and Y. JOHAR

Department of Chemistry and "J. Stefan" Institute
"E. Kardelj" University of Ljubljana
Ljubljana, Yugoslavia

ABSTRACT

Cross-linked 4-vinylpyridine-styrene beads (PVPS) containing various amounts of pyridine rings were synthesized and reaction with methyliodide and peroxyacetic acid gave corresponding N-methylpyridinium salts and N-oxides with more than 92% of the pyridine rings being transformed. PVPS formed stable complexes with bromine and chlorine in the ratio 1:1, and when a higher amount of halogen was used, complexes with two molecules of halogen on each pyridine were formed. Similar complexes were also formed with PVPS-N-oxides in the presence of bromine and chlorine, while the reaction of PVPS-hydrohalide with bromine and chlorine resulted in hydrobromide perbromide and hydrochloride perchloride resins. The chemical activity of halo-substituted resins was tested in the reaction with 1,1-diphenylethylene. Chloro-substituted resins are very stable, while bromo-substituted beads gave bromoalkene, dibromide, and alkoxybromide, depending on the structure of the reagent, solvent, and reaction temperature.

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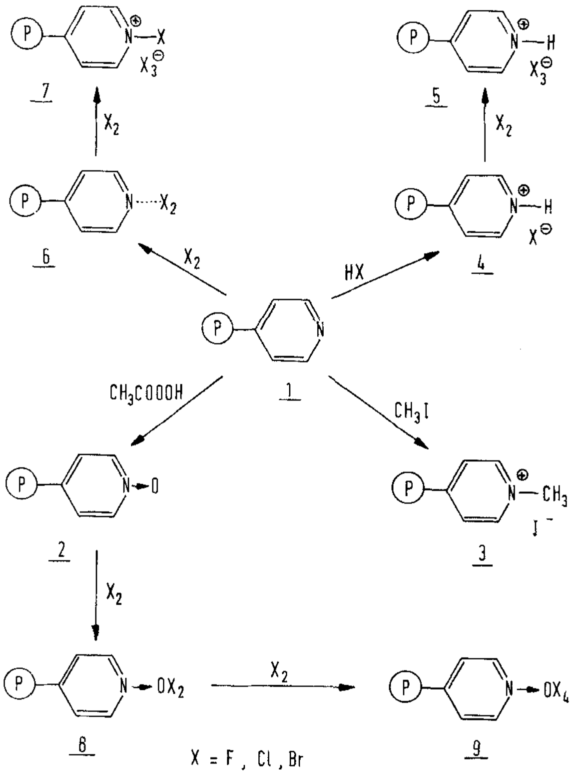
Cross-linked polystyrene beads have found a wide range of use in organic chemistry for the preparation of reagents and catalysts, while cross-linked polyvinylpyridine or cross-linked copolymers with styrene and vinylpyridine have received much less attention. On the other hand, it is well known that pyridine has wide application in organic synthesis by itself or in conjunction with other reagents. Recently it has been demonstrated that polyvinylpyridine could be used as an HCl acceptor [1], poly(vinylpyridinium hydrobromide perbromide) resins as brominating agents [2], poly(vinylpyridinium chlorochromate) as an oxidizing agent [3], poly(vinylpyridine borane) complex as a reducing agent [4], polyvinylpyridine as matrices for protein immobilization [5], and the Cu-complex with polyvinylpyridine as a catalyst for polymerization [6].

In our continued interest in the preparation of halo-substituted organic molecules with polymer supported reagents [7], we found it relevant to study the effect of polymer resins on the properties of halogen complexes. We now report the preparation of a copolymer of 4-vinylpyridine with styrene in the presence of divinylbenzene (2%). Polymer with various amounts of pyridine nucleus were prepared in order to establish the effect of the structure of the polymer on the chemical reactivity and also to find the most resistant support, mechanically and chemically. The chemical reactivity of PVPS beads with various amounts of pyridine rings was investigated by reaction with methyl iodide and peroxy acetic acid (Scheme 1). In both cases more than 90% of the pyridine rings were chemically modified and the degree of chemical transformation was followed by elemental analysis and IR spectroscopy. The changes in IR spectra for resins containing 40-43% of pyridine rings are presented in Fig. 1, where in the case of quaternization with methyliodide the signal for $\nu_{C=N}$ is shifted from 1580 to 1620 cm^{-1}, this difference being very important for further characterization of the nature of the complexes. In the case of N-oxide resins, a new strong signal at $\nu = 1220$ cm^{-1} proved the chemical transformation.

We prepared different types of halogen complexes, as shown in Scheme 1. Introduction of a mixture of fluorine and nitrogen through a suspension of beads 1 or 2 or 4 at room temperature resulted in a change of color of the polymer to green-yellow, while elemental analysis showed the presence of only 1-2% of fluorine, the resins being very stable at room temperature. The reaction of Resins 1 or 2 with chlorine or bromine gave two types of complexes, depending on the concentration of halogen. The use of equivalent amounts of halogen, calculated on the basis of the pyridine rings, resulted in the formation of a 1:1 complex as shown by elemental analysis, while the use of excess halogen resulted in the formation of 1:2 complexes. Reaction of PVPS-hydrogen chloride (4, X = Cl) or hydrogen bromide (4, X = Br) with chlorine or bromine gave the corresponding PVPS-hydrogen halide-perhalide complexes. The differences in IR spectra of the three types of PVPS complexes with bromine are presented in Fig. 2. It is evident that in the case of the bromine 1:1 Complex 6,



SCHEME 1

only a small shift of $\nu_{C=N}$ is observed, while in the case of the 1:2 bromine complex a very similar IR spectrum to that of the hydrogen bromide-perbromide complex was observed, i.e., $\nu_{C=N} = 1620\ cm^{-1}$, and this shift could also be compared to the shift observed for the product of the reaction of Resin 1 with methyliodide. The observed data could be explained by postulating that in the case of equimolar amounts of halogen a complex is formed, while in the case of excess halogen a polymer salt is formed.

Further, we investigated the chemical reactivity of chloro, bromo, and fluoro Resins 5, 7, or 9 with 1,1-diphenylethylene. Under various reaction conditions and in various solvents we found that all resins containing fluorine or chlorine are very stable. On the other hand, all resins containing bromine are reactive even at room temperature. Contrary to results mentioned in the literature [2] where it has been reported that the polyvinylpyridine-hydrobromide-perbromide complex is completely unreactive in chloroform or carbon tetrachloride,

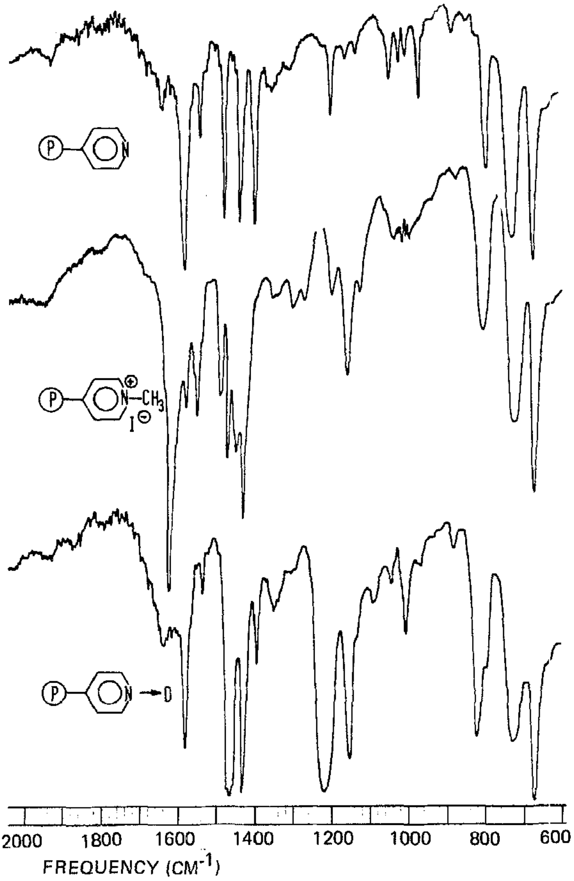


FIGURE 1

we found that all Resins 5, 7, or 9 are very active in chloroform and methylene chloride. It is interesting that it was found that bromination of alkenes proceeds successfully only in methanol [2] and no evidence for the formation of methoxy derivatives was given. We have also studied the reactions in methanol and found that large amounts of methoxy derivatives were formed. The effect of the structure of the brominating agent, solvent, temperature, and the reaction time on the bromination reaction with 1,1-diphenylethylene is presented in Scheme 2. In general, the reactivity of the brominating agent increases in the order 7 < 9 < 5. The formation of 1,1-diphenyl-2-bromoethene (12) could be explained by elimination of hydrogen bromide from 1,2-dibromo-1,1-diphenylethane (11) or by

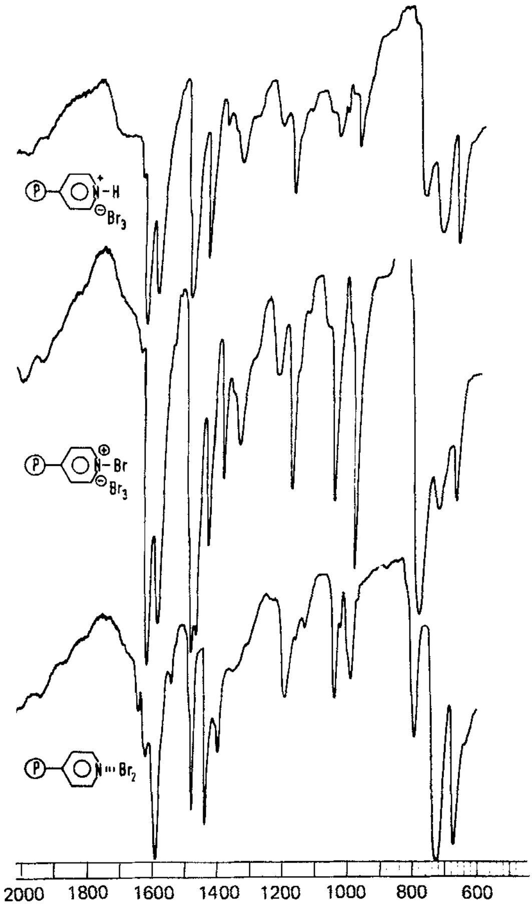


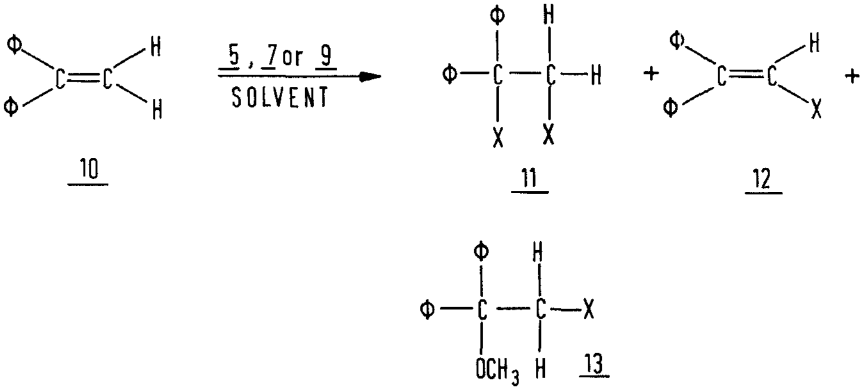
FIGURE 2

an addition elimination process. The results confirm both of the possibilities.

EXPERIMENTAL

Preparation of Cross-Linked 4-Vinylpyridine-Styrene Beads (PVPS)

In a 2-L four-necked flask equipped with reflux condenser, thermometer, stirrer, and inlet for oxygen-free nitrogen, 300 mL of 0.1%



VARIATION IN COMPOSITION OF PRODUCTS FROM ADDITION OF BROMINE TO 1,1- DIPHENYLETHYLENE

REAGENT	SOLVENT	TEMP. °C	TIME min	11	12	13
7 X = Br	$CHCl_3$	25	210	7	93	
	$CHCl_3$	62	90		100	
	CH_3OH	25	120			100
	CH_3OH	65	90		75	25
9 X = Br	$CHCl_3$	25	20	50	50	
	$CHCl_3$	25	210	4	96	
	$CHCl_3$	62	90		100	
	CH_3OH	25	120	11	20	69
	CH_3OH	65	90	6	41	53
5 X = Br	$CHCl_3$	25	20	50	50	
	$CHCl_3$	25	210	7	93	
	$CHCl_3$	62	90		100	
	CH_3OH	25	120	15	37	48
	CH_3OH	65	90	15	34	51
	CH_3OH	65	150	8	77	15

SCHEME 2

water solution of polyvinyl alcohol, 100 mL of water, 0.54 g of azabisisobutyronitrile, 6.7 g of divinylbenzene (50% in ethylvinylbenzene), and various amounts of styrene and 4-vinylpyridine were stirred and heated so that the reaction mixture reached 70°C in 1 h. The stirring velocity was then increased and the heating continued for 3 h at 70°C and finally for 1 h at 90°C. The polymer carrier was filtered off; washed with water, acetone, chloroform, and methanol; dried in air; and finally for 2 h at 80°C. Various amounts of product were isolated, depending on the ratio of styrene:4-vinylpyridine. When 136 g of styrene and 98 g of 4-vinylpyridine were used, 144 g of product was isolated, containing 40-43% of pyridine rings; 136 g of styrene and 40 g of 4-vinylpyridine gave only 60 g of product containing 20-22% of pyridine rings; 136 g of styrene and 14.7 g of 4-vinylpyridine gave 115 g of polymer carrier with 7.5-8.5% of pyridine rings; 136 g of styrene and 5 g of 4-vinylpyridine gave 122 g of product with 4-4.5% of pyridine rings.

Quaternization of PVPS

1 g of PVPS, containing 3.8 meq of pyridine rings per gram of beads, was suspended in 8 mL of dry methanol and 2 g of methyliodide was added. The mixture was heated under reflux for 2 h, the product was filtered off, washed with methanol, dried in air, and finally at 40°C for 2 h. 1.4 g of product was isolated, containing 2.6 meq of pyridine rings per gram of beads, which means that 95% of the pyridine rings were quaternized. A similar degree of transformation was observed in the reactions of other beads containing various amounts of pyridine rings.

Oxidation of PVPS

10 g of PVPS containing 3.8 meq of pyridine rings per gram was suspended in 60 mL of chloroform, cooled to 0°C, and peroxyacetic acid in chloroform (22 g of aceticanhydride and 5.2 g of 90% H_2O_2) was slowly added. The reaction mixture was stirred for 1 h at 0°C and then for 2 h at room temperature. The polymer was filtered off, washed with chloroform, dried, suspended in 200 mL of 2 N NaOH, heated to 50°C, and stirred for 0.5 h. The product was filtered off; washed with water, acetone, and chloroform; and dried to constant weight. 10.2 g of product, containing 3.45 meq of pyridine rings per gram of beads, was isolated, which means that oxidation took place on more than 95% of the pyridine rings. A similar degree of N-oxidation was also observed in reactions of other beads containing various amounts of pyridine rings.

Preparation of Halogen Complexes 7 with PVPS

In all the cases described, beads containing 3.8 meq of pyridine rings per gram of polymer were used.

Reaction with Fluorine

5 g of PVPS was suspended in 50 mL of chloroform and under stirring a mixture of 2% of fluorine in nitrogen was introduced at room temperature. After 20 mmol of fluorine had been introduced, the product was filtered off, washed with chloroform, and dried to constant weight at room temperature. 5.3 g of polymer containing 3.4 meq of pyridine rings per gram of beads was isolated, the content of fluorine being only 1.74%. The complex was very stable at room temperature.

Reaction with Chlorine

5 g of PVPS was suspended in 50 mL of chloroform and under stirring chlorine gas was introduced at 0°C until the yellow color of chloroform persisted. The reaction mixture was stirred for 1 h at room temperature, the product was filtered off, washed with chloroform, and dried to constant weight at room temperature. 6.1 g of polymer containing 30.8% of chlorine was obtained. The high percentage of chlorine can be explained by the fact that more than 60% of pyridine rings are occupied by four chlorine atoms. Reaction with a smaller amount of chlorine resulted in the formation of only a 1:1 complex.

Reaction with Bromine

5 g of PVPS was suspended in 50 mL of chloroform and under stirring 5 g of bromine was added and stirred for 1 h at room temperature. The polymer was filtered off, washed with chloroform, and dried to constant weight at room temperature. 8 g of beads, containing 50.1% of bromine, was isolated, which means that more than 60% of the pyridine rings are occupied by four bromine atoms. The use of an equivalent amount of bromine resulted in the formation of a 1:1 complex.

Preparation of Halogen Complexes (9) with PVPS-N-Oxide (2)

In all the cases described, beads containing 3.45 meq of pyridine rings per gram of polymer were used. The work-up procedure for the preparation of fluorine, chlorine, and bromine complexes was similar to those for the preparation of PVPS complexes with halogens. Resins containing the following amount of halogen were isolated:

Reaction with fluorine gave beads containing 1.43% of fluorine.
Reaction with an excess of chlorine gave beads containing 32% of chlorine.
Reaction with bromine gave beads containing 47.4% of bromine.

The high chlorine and bromine contents can again be explained by the fact that more than two atoms of halogen are bonded to the pyridine N-oxide ring. When equivalent amounts of chlorine or bromine were used, 1:1 complexes were obtained.

Preparation of Polyvinylpyridinium Hydrohalide Perhalide Resins

In all the cases described, beads containing 40% of pyridine rings were used.

Reaction with Hydrogen Fluoride and Fluorine

5 g of PVPS was suspended in 50 mL of chloroform and under stirring of 0°C hydrogen fluoride was introduced for 0.5 h, followed by the introduction of a mixture of 2% fluorine in nitrogen into the reaction mixture. The product was filtered off, washed with chloroform, and dried to constant weight at room temperature. 5.8 g of product containing 9.67% of fluorine was isolated.

Reaction with Hydrogen Chloride and Chlorine

5 g of PVPS was suspended in 50 mL of chloroform and 5 mL of concentrated HCl was added at room temperature and stirred for 1 h. The resins were filtered off, dried at room temperature, and suspended in 50 mL of chloroform. Chlorine gas was introduced under stirring at 0°C until the yellow color of the solvent persisted. The beads were stirred for 1 h at room temperature, filtered off, washed with chloroform, and dried at room temperature to constant weight. 6.5 g of product was isolated, containing 28.1% of chlorine, which corresponds to a degree of functionalization of more than 95%.

Reaction with Hydrogen Bromide and Bromine

5 g of PVPS was suspended in 50 mL of chloroform and under stirring 5 mL of 63% hydrogen bromide was added at room temperature and stirred for 1 h. The beads were filtered off, dried at room temperature, and suspended in 50 mL of chloroform. 2.5 g of

bromine was added at 0°C and stirred for 4 h. The product was filtered off, washed with chloroform, dried at room temperature to constant weight, and 9 g of polymer containing 41.5% of bromine was isolated, which corresponds to a degree of functionalization of more than 85%.

Reactions of Complexes 5, 7, and 9, with 1,1-Diphenylethylene

In a typical experiment we dissolved 1 mmol of diphenylethylene in 10 mL of solvent (chloroform, methylene chloride, methanol). 1 g of polymer reagent containing halogen (5, 7, or 9) was added and stirred at various temperatures (25, 62, 65°C) for various times (20 min, 5 d). The insoluble product was filtered off, washed with chloroform, the solvent was evaporated in vacuo, and the reaction mixture was analyzed by GLC, TLC, and NMR spectroscopy. It was found that under the conditions mentioned above, only reactions with bromo complexes (5, 7, 9, X = Br) gave products. The product distribution is stated in Scheme 2. The most reactive reagent is the polyvinylpyridinium-hydrobromide-perbromide complex (5, X = Br), while the least reactive complex proved to be 7 (X = Br). Products formed in the reactions were isolated in high yields by preparative GLC and TLC and characterized on the basis of spectroscopic data. Data presented in Scheme 2 are the average values of several experiments, the product distribution being determined by ^{1}H NMR spectroscopy.

Regeneration of Resins

Beads were suspended in a 2 N solution of sodium hydroxide; stirred at 50°C for 1 h; washed with water, acetone, and chloroform; and dried at room temperature to constant weight. No loss of polymer activity for further preparation of complexes was found.

REFERENCES

[1] M. L. Hallensleben and H. Wurm, Angew. Chem., 88, 192 (1976).
[2] J. M. J. Frechet, M. J. Farrall, and L. J. Nuyens, J. Macromol. Sci.-Chem., 11, 507 (1977).
[3] J. M. Frechet, J. Warnock, and M. J. Farral, J. Org. Chem., 43, 2618 (1978).
[4] F. M. Menger, H. Shinozaki, and H-C. Lee, Ibid., 45, 2724 (1980).

[5] F. Pittner, M. G. Pittner, and M. Wilchek, J. Am. Chem. Soc., 102, 2451 (1980).
[6] E. Tsuchida and H. Nishide, Macro Florence 1980, Vol. 4, p. 147.
[7] M. Zupan and A. Pollak, J. Chem. Soc., Chem. Commun., p. 715 (1975); B. Sket and M. Zupan, Synth. Commun., 6, 309 (1976); M. Zupan, Collect. Czech. Chem. Commun., 42, 266 (1977).

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