

ROLE OF THE POLYMER BACKBONE IN THE OXIDATIVE PROPERTIES
OF POLYMER - SUPPORTED DICHROMATE

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Summary

Crosslinked co/poly(styrene-4-vinylpyridine)/ (1) was converted with hydrogen bromide or alkyl bromide to a pyridinium salt (2) which was further converted in water medium to various immobilized dichromates (3) with CrO_3 . The insoluble reagent containing 0.6 - 1.0 mmol of dichromate on a gram of resin (depending on the structure of the polymer backbone) oxidized several secondary alcohols to ketones. The rate of conversion of alcohols to ketones depended on the structure of the polymer backbone, the structure of the alcohol, and the amount of water (5% or 20%) occluded in the reagent 3.

It is well established that several reagents can be modified in the presence of insoluble organic¹ or inorganic² supports, and besides the different behaviour, the work-up procedure is usually significantly im-

proved. One of the most studied organic supports is crosslinked polystyrene. However, in spite of the fact that pyridine is a very useful substrate in organic synthesis, copolymers with polyvinylpyridines are much less studied³.

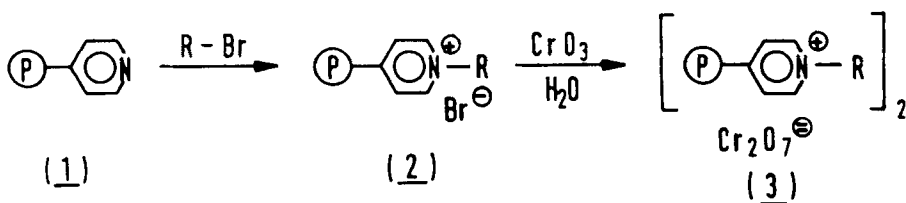
Cardillo and coworkers have found that dichromate could be bound to the ion-exchange resin Amberlyst A-26⁴, while Fréchet and coworkers reported the preparation of the following new supporting reagents: poly(vinyl(pyridinium chlorochromate))⁵ and poly(vinylpyridinium dichromate)⁶. Brunelet and Gelbard have studied the oxidation of various alcohols with CrO_3 in the presence of several polymers⁷.

In our continued interest in the preparation of polymer supported reagents based on crosslinked co/poly(styrene-4-vinylpyridine)⁸, we found it instructive to prepare several polymer supported reagents based on dichromate in order to study the effect of backbone structure and reaction conditions on the reactivity.

Results and Discussion

Crosslinked co/poly(styrene-4-vinylpyridine)/ prepared by suspension polymerization⁹ and containing 40-43% of pyridine rings (Scheme), was converted with hydrogen bromide, *n*-hexyl bromide, and *n*-dodecyl bromide to the corresponding salts (2a, 2b, 2c). It has been demonstrated by potentiometric titration¹⁰ that all the pyridine rings were functionalized. Pyridinium salts (2) were suspended in water, CrO_3 was added and the reaction mixture stirred for four hours at room temperature. The insoluble product was filtered off and washed with water until a colourless filtrate was

SCHEME



2a, 3a : R = H

2b, 3b : R = n - C₆H₁₃

2c, 3c : R = n - C₁₂H₂₅

THE EFFECT OF THE STRUCTURE OF THE REAGENT (3a - 3c), SOLVENT AND WATER ON OXIDATION OF 1-PHENYLETHANOL (REACTION TIME: 6hrs, T = 50°C)

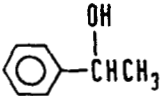
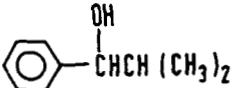
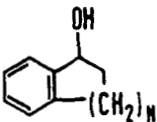
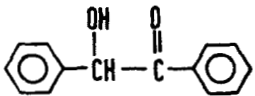
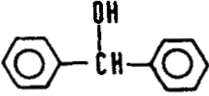
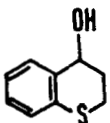
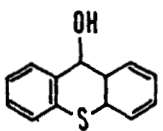
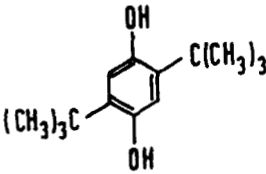
REAGENT (3)	SOLVENT	AMOUNT OF WATER	CONVERSION OF ALCOHOL
R = H	BENZENE	5%	8%
	BENZENE	20%	88%
R = n - C ₆ H ₁₃	BENZENE	5%	61%
	BENZENE	20%	31%
	TOLUENE	5%	55%
	CHLOROFORM	5%	39%
	CYCLOHEXANE	5%	36%
	CYCLOHEXANE	20%	40%
R = n - C ₁₂ H ₂₅	BENZENE	3%	65%
	BENZENE	17%	50%

achieved. The amount of dichromate bound was established by titration with $\text{Na}_2\text{S}_2\text{O}_3$ and the following loadings were found: 3a 0.8–0.95 mmol/g; 3b 0.85–1.0 mmol/g; 3c 0.6–0.8 mmol/g (established for dry supports). We first studied the effect of the structure of the backbone, the solvent polarity, and the amount of water occluded into reagent on the oxidation of 1-phenylethanol, which is presented in the Scheme. Chloroform and benzene swell the reagents 3a - 3c very well, while in toluene and cyclohexane the swelling is much poorer. The amount of water occluded plays a very important role and different behaviour of the reagents was observed. In benzene as solvent an increase in the amount of water increased the rate of oxidation of alcohol only in the case of 3a, while in the case of 3b and 3c a greater amount of water diminished the rate of conversion. Further, we have studied the effect of the structure of the alcohol on the oxidation with the hexyl substituted reagent 3b (containing 5% of water) in benzene, and the reaction conditions (reaction time and reaction temperature) leading to complete conversion of the starting alcohol are presented in the Table. The course of the reaction was followed by nmr spectroscopy, and after the usual work-up procedure, the ketones isolated were purified (crystallization or distillation; the yields are presented in the Table). The hexyl substituted reagent 3b could be regenerated and reused at least five times without any appreciable loss of activity.

Experimental Section

Ir spectra were recorded using a Perkin Elmer 727 B spectrometer, and ^1H nmr with a Jeol JNM PS 100 spectrometer with Me_4Si as internal

TABLE THE EFFECT OF THE STRUCTURE OF ALCOHOL ON OXIDATION WITH REAGENT 3B

SUBSTRATE	REACTION		YIELD OF ISOLATED PRODUCT
	TEMP. [°C]	TIME [hr]	
	80	7	80%
	80	12	85%
 <div style="display: inline-block; vertical-align: middle; margin-left: 10px;"> N = 1 N = 2 (CH₂)_N N = 3 </div>	80	20	88%
	80	8	80%
	80	20	85%
	80	8	84%
	80	8	87%
	80	8	82%
	80	8	87%
	20	2	76%

reference, while mass spectra and high resolution measurements were taken with a CEC 21-110 spectrometer. Glc analysis was carried out on a Varian Aerograph 1800 instrument and tlc on Merck Silicagel F 254 Fertigplatten. Crosslinked co/poly(styrene-4-vinylpyridine)/ and quaternary salts (2a, 2b, 2c) were prepared according to previously published procedures^{9,11}.

Preparation of Polymer Supported Dichromates 3a, 3b, and 3c

10 g of insoluble product 2a was suspended in 50 ml of water, 2.5 g of CrO_3 was added and the reaction mixture was stirred at room temperature for four hours. Insoluble resins were filtered off and washed with water until a colourless filtrate was achieved. For further investigations the resins containing different amounts of water were used, as indicated in Scheme 1. The loading of reagents 3a, 3b, or 3c with dichromate was established in the following way: a glass column was filled with the reagent, the dichromate was eluted with 3M NaOH until a colourless filtrate appeared, the filtrate was acidified with H_2SO_4 , KI was added and the liberated iodine was titrated with $\text{Na}_2\text{S}_2\text{O}_3$. The following amounts of dichromate were found: 3a: 0.8 - 0.95 mmol/g; 3b: 0.85 - 1.0 mmol/g; 3c: 0.6 - 0.8 mmol/g.

(Theoretical capacity of the fully loaded resins: mmols of Cr_2O_7^- /g:
3a: 1.35; 3b: 1.1; 3c: 0.93).

Addition and Isolation Procedures

0.5 - 1.0 mmol of alcohol was dissolved in 7 - 10 ml of solvent and the reagent 3a, 3b, or 3c, containing 0.6 - 1.2 mmol of dichromate per gram of corresponding polymer was added. The suspensions were heated at

various temperatures and for various times (see Scheme and Table). The insoluble resins were filtered off, washed with solvent, the solvent was evaporated in vacuo and the crude reaction mixture was analyzed by ^1H nmr, gic, or tlc. Ketones were purified by crystallization or distillation and their physical and spectroscopic data were in agreement with the literature.

References

1. Hodge, P.; Sherrington, D.C. "Polymer-Supported Reactions in Organic Synthesis", Wiley, London 1981; Mathur, N.K.; Narang, C.K.; Williams, R.E. "Polymers as Aids in Organic Chemistry", Academic Press, New York, 1980; Editor Ford, W.T. "Polymeric Reagents and Catalysts", American Chemical Society, Washington, DC 1986.
2. McKillop, A.; Young, D.W. *Synthesis* **1979**, 401; **1979**, 481; Cornelis, A.; Laszlo, P. *ibid.* **1985**, 909.
3. Fréchet, J.M.J.; de Meftahi, M.V. *Brit.Polym.J.* **16**, 193 (1984).
4. Cardillo, G.; Orena, M.; Sandri, S. *Tetrahedron Lett.* **1976**, 3985; Cainelli, G.; Cardillo, G.; Orena, M.; Sandri, S. *J.Am.Chem.Soc.* **98**, 6737 (1976).
5. Fréchet, J.M.J.; Warnock, J.; Farrall, M.J. *J.Org.Chem.* **43**, 2618 (1978).
6. Fréchet, J.M.J.; Darling, P.; Farrall, M.J. *J.Org.Chem.* **46**, 1728 (1981).
7. Brunelet, T.; Gelbard, G. *Nouv.J.Chim.* **7**, 483 (1983).
8. Šket, B.; Zupan, M. *J.Org.Chem.* **51**, 929 (1986).
9. Zupan, M.; Šket, B.; Johar, Y. *J.Macromol.Sci., Chem.* **17**, 759 (1982).

10. Kim, B.; Kirszensztejn, P.; Bolikal, D.; Regen, S.L. *J.Am.Chem.Soc.* **105**, 1567 (1983).
11. Metelko, M.; Zupan, M. *J.Macromol.Sci., Chem.:* in press.

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