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Oxidation of Alcohols with Chromium Complexes Supported on Polyvinyl-Pyridine Resins Influence of the Structure of the Resin on Its Performances

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SUMMARY

Various resins carrying pyridine rings have been used to support ionic or neutral chromium complexes, and oxidize selectively octanol-2 into octanone-2. The best results involve macroporous resins with large pores or non cross-linked grafted polymers, provided that grafted polymers are compatible enough with the solvent medium for the reaction.

INTRODUCTION

Although an increasing number of work is devoted to organic synthesis using reagents supported on polymers, there is not yet clear conclusions about the structure of the support which should be best suited to a given organic synthesis reaction (Hodge and Sherington... 1980). The present note is to make a contribution in that direction. It deals with the use of supported chromium complexes, both ionic and neutral, attached to a polymer carrying pyridine rings, to selectively oxidize octanol-2 into octanone-2. More general use of that system will be described elsewhere (BRUNELET et GELBARD, in press). Some results in these lines already appeared in the literature. For instance, Cainelli et al. (CAINELLI et al... 1976) have used chromate ion supported on quaternary amonium resin Amberlyst® A26 to oxidize primary and secondary alcohols. More recently, Frechet described a polymeric analogue of pyridinium chlorochromate as an effective reagent in the oxidation of alcohols into the corresponding aldehydes and ketons (FRECHET et al. 1978). In a second paper, the same authors (FRECHET et al... 1981) report improved results from the use of chromate anions on a small size gel type polymer prepared through an emulsion (actually microsuspension) technique, and which lead to complete reaction in a reasonable time without a large excess of supported reagent.

RESULTS AND DISCUSSION

The set of resin used in the present work involves :

a) a commercial gel type crosslinked polyvinylpyridine resin PVP 901 (a precursor of IONAC A 580 anion exchange resin) ;

b) macroporous resins (FP series) prepared in the laboratory (WEINGERTNER et al., unpublished) by suspension copolymerization of styrene-vinyl-4-pyridine and commercial divinylbenzene, in the presence of heptane as a diluent ;

c) resins grafted by post-polymerization of styrene and vinylpyridine onto a commercial (ES861) macroporous styrene-divinylbenzene of high surface

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area (640 m^2/g) produced by DIAPROSIM. The grafting process has been described elsewhere (BRUNELET, BARTHOLIN and GUYOT, in press).

The porous volume of these resins, in the dry state, have been measured by mercury porosimetry, and their surface area through the BET method. Results are given in TABLE I and TABLE II. For comparison, a commercial quaternary amonium resin (Amberlyst A26) has been included, for the experiments, involving ionic chromium complexes.

The use of these resins in organic synthesis involves two steps : fixation of the chromium species onto the resin, and the oxidation reaction itself. The cases of ionic and neutral complexes will be considered separately.

The fixation of ionic chlorochromate complexes has been carried out by simply contacting the resin and an excess of HCl 6N aqueous solution for a few hours ; then introduction of an excess of CrO_3 into that solution, after enough contact, the resin is filtered off, washed with acetonitrile and dried; care must be taken then to avoid the contact of moisture to make sure that the chlorochromate complex is not hydrolysed into chromate or bichromate complex of different reactivity. For the neutral complexes, CrO_3 is dissolved in acetonitrile, the resin added and 24 hrs of contact under gentle stirring is carried out before filtering, washing with acetonitrile and drying.

In both cases, the oxidation test is carried out 4 hrs at 70° C ; cyclohexane is the solvent medium and about a threefold excess of chromium is used versus the octanol-2. Results are given in TABLE I and TABLE II.

Resin	N %	Cr fixat. %		OXIDATION			Vp	S	$\bar{r}$
		calc.	exp.	Cr/Alcohol	Octanone-2 %	Recovered Octanol-2 %	cm^3/g	m^2/g	Å
PVP 901	0.71	18.7	6.3	4.5	11	65	0.3	10	600
VP 8	0.71	18.7	16	7.2	25	59	0.2	10	400
FP 8	0.52	15.8	11.3	3.1	37	48	2.4	7.7	5900
A 26	0.47	14.7	12.0	5.1	39	54	0.24	18	175

TABLE I

Oxidation of octanol-2 into octanone-2 with supported chlorochromate complexes

For the ionic complexes, (TABLE I), bad results are obtained with the gel type resins considering both chromium fixation and alcohol oxidation. Excellent yield in chromium fixation are obtained with the VP 8 resin functionalized via post-copolymerization of vinylpyridine with the residual double bond of the backbone resin. A macroporous resin, FP8, moderately crosslinked but with very high porous volume leads to good enough chromium fixation but better oxidation results, which are now comparable to those with quaternary amonium resin (BRUNELET et GELBARD, in press).

For the neutral complexes (TABLE II), the chromium fixation is only efficient when macroporous resins with high porous volume are used. In all other cases, the yield is rather low. The same macroporous resin also gives very good results in the oxidation process. For grafted resins, better results

TABLE II

Oxidation of octanol-2 into octanone-2 with supported neutral chromium complexes

Resin	DVB %	N %	Vp cm^3/g	S m^2/g	$\bar{r}$ Å	Chrom. fix.		Oxidation		
						calc.	exp. %	Cr/Alcohol	Octanone-2 %	Recovered octanol-2 %
PVP901	-	0.71	0.3	10	600	21.5	2.3	3.5	5	65
VP8	-	0.71	0.2	10	400	21.5	2.5	4.8	27	32
SVP4[a)]	-	0.19	0.3	16	375	8.3	2.8	3.3	58	27
FP6	40	0.35	1.0	114	175	13.5	2.3	3.8	10	54
FP8	10	0.52	2.4	7.7	5900	17.8	13.1	3.0	80	6
FP12	40	0.22	1.6	51	1040	9.4	6.4	2.2	74	17

[a)] SVP 4 results from grafting copolymerization of styrene and vinylpyridine onto ES861 are obtained when vinylpyridine is more diluted (SVP 4 compared to VP 8). Anyway, the gel type resin is very poor.

From these results, it may be concluded that the site accessibility, necessary for both fixation of the active reagents and their efficient use, can be obtained by two different ways :

a) compatibility with the reaction medium : this is illustrated in the case of the ionic complexes by the behavior of VP8 in the chromium fixation complex : in that resin, polyvinypyridine, grafted onto the resin is practically uncrosslinked and swells very well in the HCl 10N solution. The gel type PVP 901 with the same site contents is not accessible enough. Another example is the comparison of VP8 and SVP4 in the oxidation process with the neutral complex : here, the medium is mostly cyclohexane which, at 70° C, is rather a good solvent for polystyrene but remains a non-solvent for polyvinylpyridine. In both examples, the sites are located in non-crosslinked regions.

b) presence of large pores : the best illustration of that statement is given by the behaviour of FP8 in all the four cases. As shown by figure 1, that resin has a double distribution of large pores ; FP 12 also has a distribution of large pores but is more crosslinked. The distribution of pores of FP6 on the other hand, does not show pores larger than 900 Å.

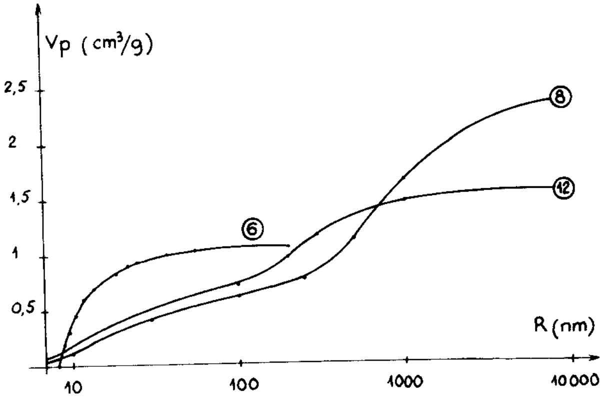

Figure 1 - Pore size distribution (by mercury porosimetry) of dry resins FP6, FP8 and FP12

Most of the functional polymers, either gel type or macroporous, have functional groups inside the bulk of the polymer, more than onto their surface. The present study suggests that it could be interesting, for the future, to have a backbone macroporous resin with large pores onto which a non-crosslinked functional polymer is grafted. It may be recalled at that moment that MORAWETZ (1979) recently observed that "it might be advantageous to use linear polymers swelling to a desirable degree in the reaction medium.... rather than polymers rendered insoluble by crosslinking". What we suggest is to graft these linear polymers onto a support with high physical accessibility.

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