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POLYMERS AS REAGENTS AND CATALYSTS - PART 29 THE ROLE OF POLYMERIC MEDIATOR STRUCTURE IN ELECTROCHEMICAL OXIDATION[1]

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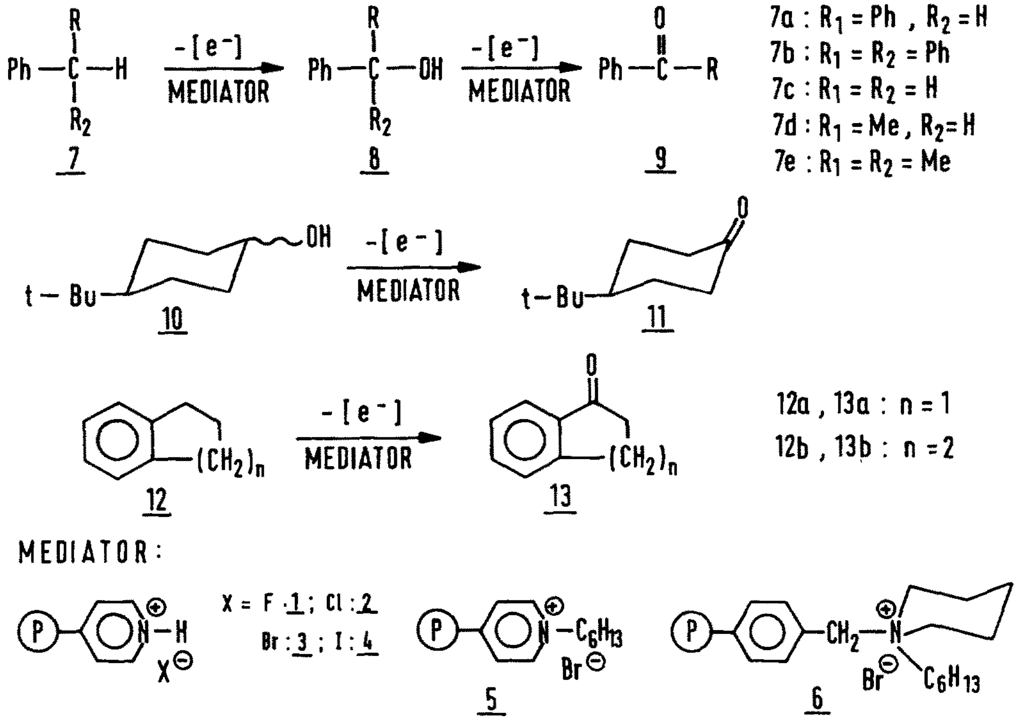
Abstract - Electrochemical oxidations of phenylsubstituted alkanes and alcohols in the presence of various polymeric mediators were studied. The effect of halide (X=. F, Cl, Br, I) bonded to an insoluble resin, on the oxidation of diphenylmethane and triphenylmethane was investigated and poly(styrene-co-4-vinylpyridinium) chloride was found to be the most effective In contrast, crosslinked poly(styrene-co-4-vinylpyridinium) bromide was the most effective mediator in the oxidation of alcohols to ketones, where also the influence of polymer matrix, i e., functionalized polystyrene or poly(styrene-co-4-vinylpyridine) bearing bromide ion, is most evident The structure of the substrate played an important role in electrochemical oxidations in the presence of polymer mediators.

Electrochemical functionalisation of organic molecules is an important area of organic chemistry[2,3], further enhanced by the developement of various types of electrochemical mediators[4,5]. Its greatest disadvantage is the necessity of separation of the electrolyte and mediator from reaction products, which was partly avoided with the development of polymer-modified electrodes[5,6]. Howewer, the possible use of insoluble organic polymers as electrolyte or mediator is being investigated. Kawabata and coworkers found that crosslinked poly(styrene-*co*-4-vinylpyridinium) bromide could be used instead of the usual soluble electrolyte in electrochemical oxidations of various alcohols, while complex reaction mixture resulted in the presence of poly(styrene-*co*-4-vinylpyridinium) chloride[7]. Variation of halide in insoluble, polymer-supported salt also proved important in the conversion of alkenes to epoxides[8], while the oxidation of phenylsubstituted alkanes was enhanced by the combination of two resins or by the solvent variation[9]. Similarly, bromide-containing resins were also more selective in the electrochemical oxidation of sulphides to sulphoxides, where sulphone was also formed when a chloride-containing resin was used[10].

The functionalisation of saturated carbon atoms is a challenging problem in organic chemistry. We focused our study on electrochemical oxidations of phenylsubstituted alkanes as well as alcohols in the presence of polymer bound mediators. We were primarily interested in the effect of the polymer backbone structure and the halide present as well as the structure of the organic molecule.

RESULTS AND DISCUSSION: We first studied the effect of halides bound to crosslinked poly(styrene-*co*-4-vinylpyridine) (40-43% of pyridine rings, 2% DVB). In a typical experiment, 5 mmol of diphenylmethane (7a) was dissolved in 15 ml of solvent mixture. 3.5 g of polymeric mediator (Scheme, 1-6) was added and after 0.5 hour at 50°C, the charge of 2.2±0.1 F/mol was introduced. The formation of diphenylmethanol (8a) and benzophenone (9a) was established. The effect of halide

SCHEME :



on product distribution is presented in Table 1. Besides products 8a, 9a and the starting material, up to 5% of other products, depending on the mediator, was formed. In the first case studied, chloride resin (2) was the most effective, while oxidation in the presence of iodide resin (4), was the least effective, displaying the highest selectivity of oxidation to alcohol Furthermore, the effect of polymer backbone structure on the oxidation of diphenylmethane (7a) (Table 1) was studied and no significant differences between three bromide-bearing resins (3, 5, 6) were established. Electrochemical oxidation of triphenylmethane (7b) in the presence of polymeric mediators led to the corresponding alcohol (8b), and surprisingly, in the presence of fluoride and chloride anion-containing polymer (1, 2), further oxidation to benzophenone (9b) took place. Differences in the effectiveness of polymeric mediators are more pronounced in the oxidation of triphenylmethane than in the case of diphenylmethane (Table 1). The effect of the halide present was established in oxidations of alcohols (Table 1), where the bromide resin 3 was the most effective. The course of oxidation was also influenced by the polimer backbone structure, especially in the case of 4-t-butylcyclohexanol.

Finally, we studied the effect of the structure of the organic molecule on the functionalisation of the saturated carbon atom in the presence of poly(styrene-*co*-4-vinylpyridinium) bromide (3) (Table 2). In the oxidation of indan and tetralin, only the formation of ketone was confirmed in addition to about 20% of other products, while in the case of tetralin, 3% of 1-naphthol was also established. Table 2 also shows the effect of the alcohol structure on the oxidation.

TABLE 1: The effect of the structure of the polymeric mediator on the oxidation of phenylsubstituted methanes and alcohols[a].

SUBSTRATE	Ph_2CH_2 (7a)		Ph_3CH (7b)		Ph_2CHOH (8a)	OH[c] t-Bu
MEDIATOR	$\frac{8a+9a}{7a+8a+9a}$	$\frac{9a}{7a+8a+9a}$	$\frac{8b+9b}{7b+8b+9b}$	$\frac{9b}{7b+8b+9b}$	$\frac{9a}{8a+9a}$	$\frac{11}{10+11}$
	% (rel)[b]	%	% (rel)[b]	%	% (rel)[b]	% (rel.)[b]
1	41 (1.12)	12	30 (0.81)	11	60 (0.86)	12 (0.30)
2	54 (1.45)	13	51 (1.38)	5	65 (0.93)	14 (0.35)
3	37 (1)	16	37 (1)	-	70 (1)	40 (1)
4	32 (0.87)	5	3 (0.86)	-	19 (0.27)	<1
5	34 (0.93)	14	37 (1.00)	-	52 (0.74)	34 (0.85)
6	41 (1.11)	16	41 (1.11)	-	55 (0.79)	12 (0.30)

a 5.0 mmol of substrate, 3.5 g of polymeric mediator, 15 ml of solvent (MeCN:H_2O:AcOH=9:3:1 v/v). Temperature: 50°C, charge passed: 2.2±0.1 F/mol; current 50 mA. Reaction mixtures were analysed by GC and HPLC. b Relative conversions normalised to conversion with 3. c Mixture of 37.8% cis and 62.2% trans isomer.

The present study confirms that insoluble polymer beads could be used as the electrolyte for electrochemical oxidation of organic molecules, which simplifies the isolation procedure and can lead to the design of continuous flow electrochemical reactors. However, much more work is needed to understand the role of the polymer backbone and the active site in the insoluble polymeric mediator on the functionalisation of organic molecules.

TABLE 2: The effect of the structure of phenylsubstituted alkanes on electrochemical oxidation in the presence of crosslinked poly(styrene-*co*-4-vinylpyridinium) bromide 3[a].

SUBSTRATE		PRODUCT COMPOSITION[b]		
		$\frac{8+9}{7+8+9}$	rel[c]	$\frac{9}{7+8+9}$
Toluene	7c	4	0.03	4
Ethylbenzene	7d	38	1	24
Isopropylbenzene	7e	51	1.34	-
Diphenylmethane	7a	37	0.97	16
Triphenylmethane	7b	37	0.97	-
Indan	12a		1.13	43
Tetralin	12b		1.03	39
Benzyl alcohol	8c		0.60	39
1-Phenylethanol	8d		1	65
Diphenylmethanol	8a		1.08	70
4-t-Butylcyclohexanol	10		0.61	40

a Procedure the same as in Table 1. b 8 alcohol, 9 ketone. Determined by GC, HPLC or NMR. c Relative conversions normalized to conversion of ethylbenzene for hydrocarbons and of 1-phenylethanol for alcohols.

EXPERIMENTAL SECTION: All electrolyses were conducted at constant current with an Iskra MA 4171 power supply. IR spectra were recorded with a Perkin Elmer 1310 spectrometer, ^{1}H NMR spectra with a Varian EM 360 L instrument, with Me_4Si as an internal reference. GC analyses were carried out on a Varian Model 3700 and HPLC on Milton Roy chromatograph, with the use of a Milton Roy CI 10 B integrators.

Preparation of Insoluble Polymeric Mediators: Crosslinked poly(styrene-*co*-4-vinylpyridinium) halides were prepared from crosslinked poly(styrene-*co*-4-vinylpyridine) (40% of pyridine rings, crosslinked with 2% of DVB) and the appropriate acid[11]. Mediators $\underset{\sim}{5}$ and $\underset{\sim}{6}$ were prepared according to known procedures[12,13].

Electrochemical Oxidations - General Reaction Procedure: Electrolyses were carried out in a 20 ml jacketed glass reactor, equipped with a magnetic stirrer. Platinum electrodes (10*10*1 mm) were placed in the cell parallel to each other about 5 mm apart. 5.0 mmol of substrate and 15 ml of solvent ($MeCN:H_2O:AcOH = 9:3:1$ v/v) were placed in the reactor and 3.5 g of insoluble polymer beads ($\underset{\sim}{1}$-$\underset{\sim}{6}$) were added under stirring. After thermostating the reaction mixture at 50°C for 30 minutes, a 50 mA electric current was passed through the cell until the electricity introduced reached 2.2 ± 0.1 F/mol. The crude reaction mixtures were: **A.** diluted with ethanol, the polymer beads filtered off, washed with ethanol and the filtrate and combined washings poured into water. The products were extracted into chloroform, the chloroform layer washed water, dried over anhydrous sodium sulphate and evaporated under reduced pressure. Reaction mixtures were analyzed by GC, HPLC or ^{1}H NMR spectroscopy. **B.** the polymer beads were filtered off and the crude reaction mixture analyzed by GC.

Oxidation of: ***Diphenylmethane***: procedure A; GC: FFAP (5%), 220°C; ***Triphenylmethane:*** procedure A; HPLC: Spherisorb S 10 ODS 1, $MeCN:H_2O = 7:3$; ***Diphenylmethanol***: procedure A; GC: FFAP (5%), 220°C; ***4-t-Butylcyclohexanol***: procedure A; GC: FFAP (5%), 140°C; ***Toluene***: procedure B; GC: OV-17 (10%), 60-230°C; ***Ethylbenzene***: procedure B; GC: OV-17 (10%), 90-230°C; ***Isopropylbenzene***: procedure B; GC: OV-17 (10%), 100-220°C; ***Indan***: procedure B; GC: OV-17 (10%), 120-230°C; ***Tetralin***: procedure B; GC: OV-17 (10%), 120-230°C; ***Benzyl alcohol***: procedure A; FFAP (5%), 120-230°C; ***1-Phenylethanol***: procedure A; ^{1}H NMR.

The spectroscopic and chromatographic data of known compounds are in agreement with those of the authentic samples and those found in the literature.

References:

1. Part 28: Zupan, M.; Šegatin, N. *Synthetic Comm.* 1991, in press
2. Ed.: Baizer, M. M. "Organic Electrochemistry", Marcel Dekker: New York, 1973
3. Shono, T. "Electroorganic Chemistry as a New Tool in Organic Synthesis", Springer: Berlin, 1984
4. Torii, S. "Electroorganic Syntheses", part 1, VCH: Weinheim, 1985
5. Kyriacou, D. K.; Jannakoudakis, D. A. "Electrocatalysis for Organic Synthesis", J. Wiley & Sons: New York, 1986
6. Fry, J. A.; Britton, W. E. "Topics in Organic Electrochemistry", Plenum: New York, 1986
7. Yoshida, J.; Nakai, R.; Kawabata, N. *J. Org. Chem.* 1980, $\underset{\sim}{45}$, 5269
8. Yoshida, J.; Hashimoto, J.; Kawabata, N. *J. Org. Chem.* 1982, $\underset{\sim}{47}$, 3575
9. Yoshida, J.; Ogura, K.; Kawabata, N. *J. Org. Chem.* 1984, $\underset{\sim}{49}$, 3419
10. Yoshida, J.; Sofuku, H.; Kawabata, N. *Bull. Chem. Soc. Jpn.* 1983, $\underset{\sim}{56}$, 1243
11. Johar, Y.; Zupan, M.; Sket, B. *J. Chem. Soc. Perkin Trans. I.* 1982, 2059
12. Metelko, M.; Zupan, M. *J. Macromol. Sci.- Chem.* 1989, $\underline{A26}$, 715
13. Metelko, M.; Zupan, M. *Synthetic Comm.* 1988, $\underset{\sim}{18}$, 1821