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# ORGANIC SYNTHESES WITH FUNCTIONALIZED POLYMERS:
## I. PREPARATION OF POLYMERIC SUBSTRATES AND ALKYLATION OF ESTERS.

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SOME advantages of the use of polymeric substrates in general organic synthesis have been recently explained and exploited[1,2] in the acylation and Dieckmann cyclization of aliphatic esters. This fact has prompted us to report our results in this field.

We have employed two approaches for the preparation of the required functionalized polymer (that of *p*-(2-hydroxyethyl)polystyrene (**I**) is given as example):

a) Copolymerization of styrene, *p*-divinylbenzene (DVB) and *p*-functionalized styrene, in a ratio depending on the desired cross-linking and "dilution" of the functional group.

Thus, pearl copolymerization of a 1:7 *p*-vinylphenetyl alcohol[3]: styrene mixture with 2% DVB afforded white solid beads of **I** which showed free and associated OH stretching bands in the ir spectrum (KBr). **I** was also obtained by pearl copolymerization of a 1:7 *p*-vinylphenetyl acetate:styrene mixture with 2% DVB, followed by hydrolysis with aqueous NaOH-dioxane. (It was thought that by avoiding possible intermolecular hydrogen-bond associations of the monomer, a more regular dilution of the functionalization would be attained).

b) Direct functionalization of cross-linked polystyrene by the sequence: *p*-bromination, metalation and reaction with the appropiate functionalizing agent. A stoichiometric control of the *p*-bromination step was achieved by using $Tl(AcO)_3$ as catalyst and $CCl_4$ as solvent[4]. When conventional aromatic bromination catalysts were used unreproducible results were obtained[5].

Thus, 24 g of cross-linked polystyrene and 3.8 g of 42% $Tl(AcO)_3$ were suspended in 400 ml of $CCl_4$; to this mixture, 4.8 g of bromine were slowly added at room temperature, and after complete decoloration, the polymer was washed with aq.HCl-dioxane, water, methanol, dioxane and ether, and dried. Elementary analysis showed 9.7% of bromine. The brominated polymer was treated at -13°C with excess of *n*-butyl lithium in toluene, washed with the same solvent, reacted with ethylene oxide in toluene, and hydrolyzed with aq.HCl-dioxane. After washing thoroughly with water-dioxane, methanol and ether, the polymeric beads were dried, showing the same ir spectrum as the hydroxylic polymer obtained by method a).

As a first application of polymeric substrates in organic synthesis, we have studied the direct alkylation of p-(2-hydroxyethyl)polystyrene esters of type Ⓟ-$CH_2CH_2OCOCHR_1R_2$. We selected the particular polymeric alcohol I to avoid the benzylic nature of esters prepared from chloromethylated polystyrene[1,2].

The polymer ester of isobutyric acid (0.2 mmol of ester/g of polymer) was prepared by reaction of I with isobutyryl chloride. This polymer was swelled in benzene and an equivalent amount of sodium triphenylmethylide in ether was slowly added and the mixture stirred until disappearance of the red color of the base (2-3 hrs); then, two equivalents of benzyl chloride in benzene were added and the mixture stirred overnight at room temperature. The polymer was filtered, washed successively with benzene, ether, water-dioxane, dioxane and ether , and dried. Upon hydrolysis in refluxing aq.KOH-dioxane (60 hrs), a mixture of 80% unreacted isobutyric acid and 20% benzyldimethylacetic acid was obtained[6].

At the present we are studying the alkylation of esters having more than one α-hydrogen and the Dieckmann cyclization reaction of esters of type Ⓟ-$CH_2\cdot CH_2OCO(CH_2)_nCOOC_2H_5$.

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