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POLYMERS FOR CATALYTIC CATION RADICAL CHEMISTRY

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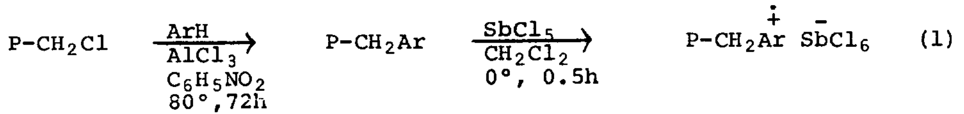
Abstract: Cation radical polymers which have cation radical functions at up to 5% of the poly(styrene) monomer sites have been prepared, and their effectiveness in catalyzing the cation radical Diels-Alder reaction is demonstrated.

Ionization of neutral singlet (NS) molecules forms cation radicals (CR's). The synthetically useful chemistry of CR's is a major current emphasis in this laboratory. Because of the reciprocal relationship of CR's with the familiar NS chemical set, they are numerous and their chemistry potentially quite diverse and important. For most synthetic purposes, chemical ionization methods are more attractive than the radiative methods. Such oxidants as H_2SO_4, $SbCl_5$, BF_3, $AlCl_3$, and Ce^{4+} have been successfully employed in chemically generating CR's.[1] More recently, organic cation radical salts, such as triarylaminium salts, have been used to accomplish extremely efficient one electron transfer.[2-4] Such salts have also been used extensively in developing the cation radical Diels-Alder (CRDA) in this laboratory.[5] To further the development of CR chemistry, a series of polymer supported organic cation radicals (cation radical polymers; CRP) has now been prepared, and their characterization and effective application to CR chemistry is now reported.

The ideal CRP was envisioned as insoluble (for convenience of removal in the workup), air and moisture stable, recyclable, relatively inexpensive, synthetically convenient, and of effective equivalent weight *ca*. 1000 or less. In addition, a series of CRP's with a range of oxidation potentials for use with appropriate NS might be useful. So far as could be determined, no such reagent existed previously. For a basic, insoluble polymer framework 2% DVB cross-linked Merrifield resin (1) was adopted. Initial work focused on attaching readily ionizable aromatic substituents to this polymer frame. It was anticipated that the resulting modified poly(styrene) (2; MPS) could be converted to the appropriate CRP (3) using the antimony pentichloride-methylene chloride reagent.

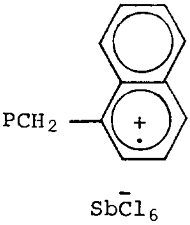


$$\text{P-CH}_2\text{Cl} \xrightarrow[\substack{AlCl_3\\ C_6H_5NO_2\\ 80°,72h}]{ArH} \text{P-CH}_2\text{Ar} \xrightarrow[\substack{CH_2Cl_2\\ 0°,\ 0.5h}]{SbCl_5} \text{P-CH}_2\overset{\dot{+}}{\text{Ar}}\ \overset{-}{\text{SbCl}_6} \qquad (1)$$

1 2 3

P = Poly(styrene)
2% DVB cross-linked

The indicated Friedel-Crafts procedure was considered feasible so long as the aromatic substrate (ArH) was more reactive than the phenyl groups of the poly(styrene). Using 5.5 g of Merrifield resin (1.09 meCl/g; 12% of the monomer units chloromethylated, *i.e.*, 12% "loading") and 9.6 g of naphthalene (excess) a 0.79 g weight gain (93% of theoretical) was realized after washing with 1N HCl-diozane (3:5), DMF, THF, and methanol and vacuum drying. The resulting brownish polymer contained no chlorine. Conversion to the CRP (4) was accomplished using antimony pentachloride. This polymer was very dark (essentially black) and surprisingly air and moisture stable, though methanol or THF largely



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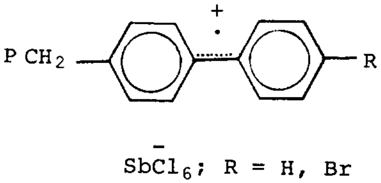

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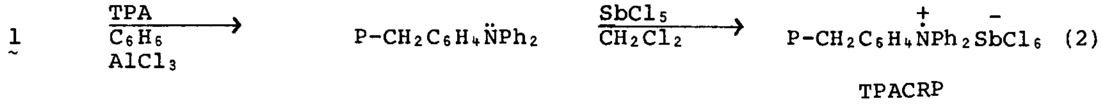
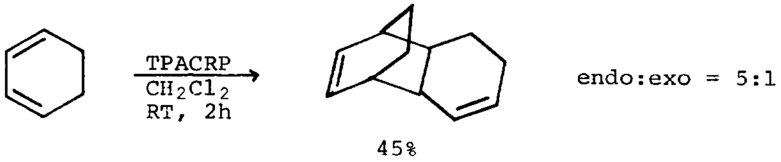
discharged its color and generated acid. Electron spin resonance spectra revealed it to be highly paramagnetic, but no hyperfines were resolvable. In one instance, a sample of the polymer which had been exposed to the atmosphere for six months still gave a very strong esr signal. Quantitative analysis of the CRP was achieved by neutron activation analysis of the antimony present and indicates 3.8% of the monomer units have antimony associated with them (i.e., 3.8% CR loading). A similar MPS was obtained from biphenyl, with a weight gain 50% of the theoretical. Chlorine was again absent and the infrared spectrum was distinct from either 1 or poly(styrene). Additional confirmation of biphenyl uptake was sought by using 4-bromobiphenyl as aromatic substrate. Elemental analysis of this MPS revealed 57% of the theoretical amount of bromine present. The properties of the CRP's (5) corresponding to these two MPS's are similar to those of the naphthalene derivative, but the degree of loading (Sb analysis; 1.5%) is appreciably less. Even poly(styrene) when treated with antimony pentachloride gave a dark, paramagnetic polymer, but antimony analysis revealed only 0.5% CR loading.

Although these results were quite encouraging, the degree of CR loading achieved was somewhat less than that targeted (≥10%). Improvement in this area was sought through the expedient of attaching to the polymer frame groups which are more easily ionizable and which would yield kinetically highly stabilized CR sites. The triphenylamine (TPA) moiety was considered virtually ideal and was attached *via* another Friedel-Crafts procedure (eq.2). The MPS thus obtained



$$\mathbf{1}\ \xrightarrow[\substack{C_6H_6\\ AlCl_3}]{TPA}\ P\text{-}CH_2C_6H_4\ddot{N}Ph_2\ \xrightarrow[CH_2Cl_2]{SbCl_5}\ \underset{TPACRP}{P\text{-}CH_2C_6H_4\overset{+\cdot}{N}Ph_2\overset{-}{SbCl_6}}\qquad(2)$$

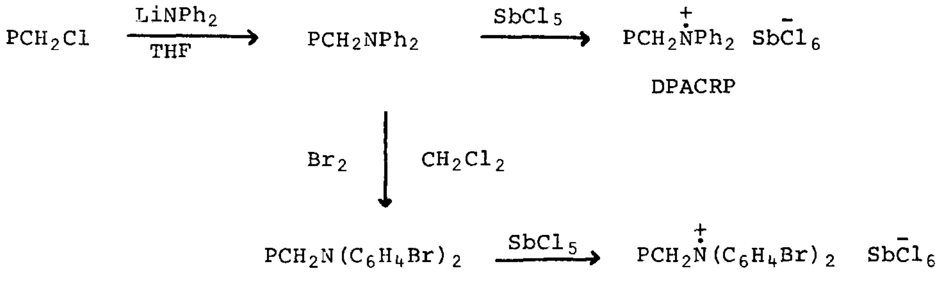
gave early indication of spontaneous CRP information by gradually turning blue when left exposed to air. Weight gain data indicated near-quantitative loading (10%). The corresponding CRP (TPACRP) is dark purple and extremely stable toward air and moisture. Antimony analysis indicates *ca.* 5% CR loading, the best achieved so far, but still short of the stated goal. Nevertheless, though it may be perhaps too sparsely loaded to recommend *generally* for stoichiometric oxidations on a synthetic scale, it is quite effective in catalytic CR processes, such as the CRDA. Instead of tris-(p-bromophenyl)aminium hexachlorostibnate ($\mathbf{6}^{+\cdot}$), the TPACRP can be used in combination with approximately 1/5 their weight of diene in methylene chloride solution to efficiently catalyze the CRDA. Workup involves filtration of



the polymer followed by quenching of persistent CR's with methoxide/methanol, and then a standard two phase aqueous workup. The advantages of the TPACRP are as follows: (1) the recovered MPS can be recharged and recycled several times, (2) no residue of inert triarylamine remains in solution to contaminate the product and (3) the TPACRP may be marginally more convenient to synthesize.

An interesting aspect of the TPACRP is that apparently the triphenylaminium function is reasonably stable when attached to a polymer framework whereas, in solution, kinetic stability is only achieved when all three *para* positions in the phenyl ring are substituted. Consequently, attempts were made to attach other aminium functions, which are kinetically unstable in solution, to poly(styrene) frameworks. An analogous diphenylaminium cation radical polymer (DPACRP) was synthesized *via* reaction of **1** with lithium diphenylamide in refluxing tetrahydrofuran, followed by treatment of the MPS with antimony pentachloride. Amine uptake in the MPS was confirmed by weight gain and nitrogen elemental analysis.

The DPACRP are, however, very inefficient catalysts for the CRDA, probably because most of the cation radical sites generated by ionization are kinetically too unstable to survive. This interpretation is confirmed by the observation that



$$\begin{tikzcd} PCH_2Cl \arrow[r, "LiNPh_2", "THF"'] & PCH_2NPh_2 \arrow[r, "SbCl_5"] \arrow[d, "Br_2"', "CH_2Cl_2"] & PCH_2\overset{+\cdot}{N}Ph_2\ Sb\overset{-}{C}l_6 \\ & PCH_2N(C_6H_4Br)_2 \arrow[r, "SbCl_5"] & PCH_2\overset{+\cdot}{N}(C_6H_4Br)_2\ Sb\overset{-}{C}l_6 \end{tikzcd}$$

DPACRP

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bromination of these same MPS (bromine in methylene chloride) produces new MPS which are oxidized to stable CRP (**7**), which catalyze the CRDA as effectively as the TPACRP. Presumably, *para* bromination confers additional kinetic stability on the DPACRP. In the same manner, reaction of **1** with lithium diethylamide followed by oxidation yields a colorless polymer containing no stable cation radical sites. However, the diethylaminated MPS decolorizes *tris*-p-bromophenylaminium hexachlorostibnate, in an indication of its ability to form cation radical sites. Both the TPACRP and DPACRP can be generated from their MPS's and $\mathbf{6}^{+\cdot}$, thus indicating that the polymer sites have a lower oxidation potential than this unsupported one.

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