

Comparison of the reactions of organic bromides and *p*-toluene sulphonates with polymeric anions

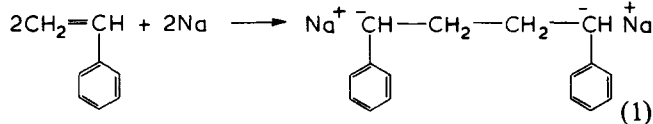
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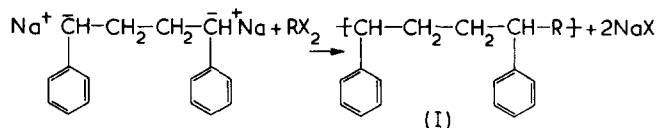
(Received 23 August 1977)

Alkyl bromides and tosylates were shown to react quantitatively with the living α -methylstyrene tetramer to yield the dialkyl adduct. Alkyl bromides also reacted with α -methylstyrene and lithium in THF to yield the dimeric adduct quantitatively, whereas only about 10% yield of this product was obtained with alkyl tosylate. This difference in behaviour was interpreted in terms of the different adsorptive powers of the two alkyl salts onto lithium metal. Aryl (phenyl) bromides and tosylates reacted with the tetramer to give only low (<5%) yields of the diaryl adduct and in both cases low molecular weight poly(α -methylstyrene) was produced. Benzene was also formed with phenyl bromide and the reaction was explained in terms of a transmetalation process. With the tosylate, the presence of phenol indicated that scission occurred at the $-\text{SO}_2-\text{O}-$ bond. The reactions of these reagents with α -methylstyrene and lithium in THF both yielded poly(α -methylstyrene) and phenyl bromide was quantitatively converted into biphenyl. Reactions controlled by competitive adsorption were invoked to explain these findings.

Some years ago a method of synthesizing regular copolymers was reported which involved an adaptation of the Szwarc 'living' polymer technique^{1,2}. This process consists of reacting a tetrahydrofuran (THF) solution of a suitable vinyl or diene monomer with alkali metal in the presence of a linking agent. It was shown that the initial reaction taking place was that of monomer with the metal to form the dimer dianion [shown in equation (1) for styrene and sodium].



This surface reaction was found to be diffusion controlled; the dimer, on diffusing away from the reaction site, could propagate further in a conventional head-tail manner until reaction occurred with the linking agent. Alkyl dihalides (RX_2) were very efficient linking agents and, under conditions of 2:1 monomer to halide molar stoichiometry, virtually no propagation occurred so that the dimer reacted directly with the halide to give copolymer of structure I, illustrated in equation (2).



The regularity of these structures was confirmed as being above 90% by using alkyl monohalides in place of dihalides, and determining the percentage dialkyl dimer formed.

Other linking agents such as diepoxides and haloepoxides were also used to give polyalcohol copolymers, although

these were less efficient and greater oligomerization took place before coupling occurred. These processes have been reviewed^{4,5}.

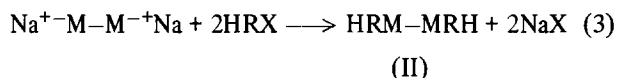
It was reported in the original publication¹ that aryl dihalides did not produce regular copolymers of structure I; the products contained only a small proportion of the aryl ligand introduced into the reaction system. The fate of the remainder was not determined, and it was suspected at the time that side reactions leading to the formation of benzyne intermediates were responsible for this behaviour. Aromatic groups could be introduced into the main chain to form copolymers, however, by using aralkyl dihalides such as *p*-xylylene dibromide, although it was shown later⁶ that with this reagent complications arose leading to copolymers possessing *p*-xylylene ligands linked together as specifically dimeric moieties in the structure. This has recently been discussed elsewhere⁷.

This communication reports work carried out to investigate these linking reactions in greater detail, and to compare the behaviour of both alkyl and aryl bromides with the corresponding *p*-toluene sulphonates (tosylates) in their reactions with polymeric carbanions, whether generated separately or *in situ* by direct reaction of monomer with alkali metal.

Alkyl tosylates are more reactive toward nucleophiles than alkyl iodides and alkylates at lower temperatures with fewer side reactions⁸. They react cleanly with Grignard reagents⁹ to give addition products analogous to those shown in equation (2), and so would be expected to behave in living polymer and similar systems in a manner closely paralleling that of the alkyl halides, although this has never been tested. In contrast, the aryl tosylates are relatively unreactive⁸, and react with Grignard reagents at elevated temperatures to yield sulphones principally⁹, and it is of

interest to examine their reactions and those of their halide analogues with carbanionic systems to compare their behaviour.

It is convenient to use monofunctional halides and tosylates in these studies since, with oligomeric dianions, termination rather than linking occurs, only small molecules are prepared and the product analysis is thereby greatly simplified. Thus, for the metathetical reaction of an organic salt (HRX) with a dimer dianion, the yield of diadduct II may be determined by g.l.c. analysis (equation 3, where M = monomer).



This approach has been employed previously to determine the efficiency of the reaction with alkyl dihalides^{3,10}, and to evaluate the microstructure of diene copolymers¹¹⁻¹³. In all these cases correspondence existed between the results obtained by this method and those calculated from direct spectroscopic examination of the copolymer prepared using the equivalent dihalide.

EXPERIMENTAL

Materials

Ethyl bromide and phenyl bromide (BDH) were used as supplied, whilst ethyl tosylate (BDH) was vacuum dried before use. Phenyl tosylate was prepared by a standard method¹⁴. α -Methylstyrene (BDH) was dried over calcium hydride and distilled under reduced pressure immediately before use. Butyllithium (Koch-Light, 15% w/w in hexane) was used as supplied. Sodium or lithium metal (BDH) was washed with 40/60 petroleum ether, dried and sliced in a stream of nitrogen directly into the reaction flask.

THF (BDH) was dried initially by standing over molecular sieves. It was then titrated with a THF solution of sodium naphthalene immediately prior to use until a faint residual green colour was obtained, after which the solvent was fractionally distilled under nitrogen.

Reactions

Two types of reaction were carried out: one in which the living tetramer of α -methylstyrene was separately generated before reaction with the halide or tosylate, and the other in which monomer and halide or tosylate, were reacted together with alkali metal in THF. They are described in that order.

Reaction with tetramer. A batch of α -methylstyrene tetramer was prepared by reacting under nitrogen 11.8 g (0.1 mol) monomer in 150 ml THF with 5 g (0.22 mol) sodium at 0°C for 3 h; 3 g (0.013 mol) of C₁₆H₃₄ was also introduced when necessary to act as a g.l.c. standard. A sample was taken, protonated and checked for tetramer formation by g.l.c. analysis. The residual solution was then separated from the excess metal by transfer into an attached burette using excess nitrogen pressure.

A sample of bromide or tosylate was then weighed into a glass receiver which was flushed thoroughly with nitrogen before attaching onto the burette. The tetramer solution was slowly titrated onto the pure reagent, which quickly dissolved, until a very faint permanent red colour was achieved. This was discharged by adding a trace of water.

G.l.c., g.p.c. and ¹H n.m.r. analyses were subsequently carried out on the product.

Reaction with alkali metal. 0.01 Mol monomer and 0.01 mol bromide or tosylate were reacted in 25 ml THF under nitrogen with excess (~0.03 mol) lithium slices at room temperature for 24 h. The solution also contained 0.004 mol C₁₆H₃₄ to act as a g.l.c. standard. The product was then analysed by g.l.c., g.p.c. and ¹H n.m.r. spectroscopy.

Gel permeation chromatography (g.p.c.)

G.p.c. analysis was carried out on a Waters Associates model ALC/GPC 301 chromatograph fitted with a differential refractometer (thermostatically controlled at 25°C) and ultra-violet (254 nm) detectors. Four styragel columns were used in sequence with porosities 10⁴, 10⁴, 10³ and 10³ Å, respectively. Elutions were carried out at ambient temperature with THF as solvent and with a flow rate of 1 cm³/min.

Gas liquid chromatography (g.l.c.)

G.l.c. was carried out on a Pye Unicam Series 105 chromatograph with flame ionization detectors. Preparative and analytical columns were packed with 2.5% OVI on 80/100 mesh 'Chromosorb G'. Temperature programmes in the range 100° to 300°C were used with these columns. Low temperature columns, used in the range 50° to 100°C, were packed with 'Porapak Q'.

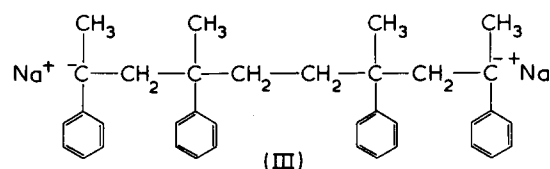
¹H nuclear magnetic resonance (¹H n.m.r.)

¹H n.m.r. spectra were recorded on a Jeol PS-100, 100 MHz spectrometer, using solutions in deuteriochloroform with tetramethylsilane as internal standard.

RESULTS AND DISCUSSION

α -Methylstyrene was chosen as a suitable monomer for the proposed experiments because: (a) the use of a vinyl monomer rather than a diene means that no analytical complications need arise due to structural isomerism of the polymerized material, and (b) this monomer has an anionic propagation rate constant much smaller than styrene so that the degree of polymerization can be more readily controlled; this is particularly important when model compound systems are used which require g.l.c. product analysis.

Basically, two types of experiments were carried out in this investigation. The α -methylstyrene tetramer dianion (structure III) was prepared in THF by conventional means¹⁵ and reacted with THF solutions of the monofunctional reagents being tested.



The products were then separated, isolated where possible by g.l.c. and analysed by ¹H n.m.r. Secondly, equimolar quantities of α -methylstyrene and monofunctional reagent were allowed to react in THF with excess lithium metal, and again the products isolated and analysed as previously. The reagents chosen were ethyl bromide and ethyl tosylate, and phenyl bromide and phenyl tosylate. They will be considered in the pairings given.

Table 1 Products of reaction (%) between organic bromides or tosylates (OTs) and (I) α -methylstyrene tetramer, and (II) equimolar α -methylstyrene and excess lithium metal

HRX	II		
	HRMMMMRH	HRMMRH	HRRH
C ₂ H ₅ Br	98	99	0
C ₂ H ₅ OTs	97	11	—
C ₆ H ₅ Br	<5	<5	98
C ₆ H ₅ OTs	<5	0	—

Ethyl bromide and ethyl tosylate

The direct reaction of ethyl bromide with the tetramer dianion yielded virtually quantitatively the corresponding diadduct (*Table 1*). Similarly, ethyl tosylate formed the same diadduct under identical conditions almost quantitatively. Thus, under homogeneous conditions, both react with strong nucleophiles almost uniquely metathetically.

The situation is dramatically altered when an analogous heterogeneous reaction is considered. In the reaction of equimolar quantities of α -methylstyrene and ethyl salt with lithium metal in THF, the ethyl bromide again gave a virtually quantitative yield of the dimer diadduct II, whereas the yield of this product with ethyl tosylate was only 11 mol %.

The difference in behaviour of these two reagents has been ascribed to the difference in their adsorptive power on to lithium metal⁷. It is supposed that vinyl monomers are strongly adsorbed on to the metal surface, where they react to form the dimer dianion which subsequently desorbs and reacts with, in this case, ethyl bromide in solution. Ethyl bromide, being entirely σ bonded, cannot compete with the adsorptive power of the easily polarizable π -bonded monomer and so an adsorbed monomer monolayer is formed over the metal, preventing access to the halide, which consequently can only react in homogeneous solution with the desorbed dianions in the manner demonstrated with the tetramer. Ethyl tosylate on the other hand possesses a permanent dipole and polarizability due to the aromaticity of the tosylate ligand, and can therefore compete effectively for adsorption sites on the metal. This allows it to become involved in competing reactions such as the Wurtz condensation reaction, and only a relatively small proportion is consequently involved in the required metathetical reaction with the desorbed dimer dianion. Some evidence of gas evolution, which could have been butane, was observed in this reaction, but this was not isolated and analysed.

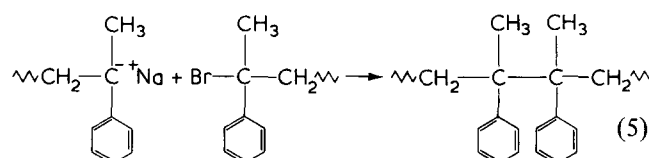
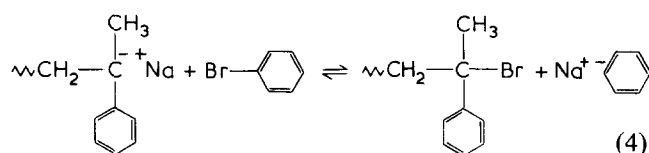
Phenyl bromide and phenyl tosylate

Addition of phenyl bromide to the living tetramer in THF caused immediate disappearance of the dark red colour characteristic of the carbanion. However, addition of the solution to methanol produced a white precipitate and, as normal tetramer adducts are soluble in this solvent, this indicated the formation of a material with a molecular weight of several thousand. This was confirmed by g.p.c. analysis which showed a broad peak with an average retention volume corresponding to a polystyrene equivalent molecular weight of about 2500. The ¹H n.m.r. spectrum of this precipitated material indicated that it was derived predominantly from the tetramer as it showed approximately equal aromatic and aliphatic absorption areas, and the characteristic high field methyl absorptions of α -methylstyrene polymers. It thus appears that the predominant effect of the phenyl bromide

reaction is to produce an appreciable increase in the molecular weight of the α -methylstyrene material, and that direct addition of the phenyl group to the terminal unit is relatively small.

The fate of the phenyl bromide was investigated initially by ¹H n.m.r. examination of the residue obtained from the methanol-THF filtrate after stripping off the solvent, but no evidence of phenyl bromide derived products was observed. The ¹H n.m.r. spectrum of the reaction mixture before precipitation, however, showed a sharp single peak at 2.7 τ which was identified as benzene, which had been stripped off with the solvents in the first investigation. This was confirmed by running g.l.c. traces of the reaction mixture under conditions suitable for separating volatile components, and the area of the benzene peak accounted almost quantitatively for the phenyl bromide added.

It thus appears that the principal reaction of phenyl bromide and the α -methylstyrene tetramer must be one of transmetallation [equation (4)], with the oligomeric bromide thus formed coupling with an unreacted anionic end to form a higher oligomer (equation 5).



The phenyl sodium produced in the equilibrium [equation (4)] eventually produces benzene, presumably either by proton abstraction from the solvent or on addition of methanol at the end of the reaction. The former possibility seems to be the more likely since analysis of experiments in which the system was terminated with ethyl bromide showed that benzene rather than ethyl benzene was still produced. The linking process [equation (5)] is terminated perhaps by a relatively slow direct metathetical reaction with phenyl bromide.

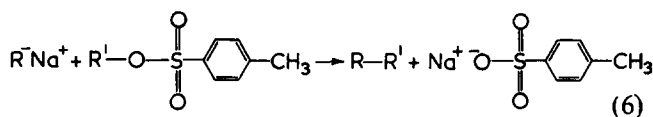
The α -methylstyrene tetramer has been linked previously by reaction with iodine¹⁶, triphenylmethyl bromide¹⁷, and vicinal dihalides¹⁸ to yield low molecular weight polymeric products, and so the process described by equation (5) is well documented. The difficulty arises in explaining why the transmetallation equilibrium should be established rather than the direct reaction to form the phenyl adduct. It is well known that halogens attached to aromatic rings are not in general readily displaced by nucleophiles, and that coupled products from these species usually arise via metal-halogen exchange¹⁹. Thus, although free energy considerations lead to the expectation that the equilibrium in equation (4) should lie well over to the left because of the resonance stabilization contribution of the benzylic anion, it is equally well established that the Wurtz condensation reaction between benzylic anions and their halides is extremely rapid¹⁹. Indeed, benzylic lithium cannot be prepared by reaction of the halide with the metal for that reason, and benzylic alkyl ethers are employed²⁰. It therefore appears that the small proportion of brominated oligomer produced by equilibration is rapidly drained away by coupling with oligomeric anions so

that only a small proportion of the latter are capped with a phenyl ligand.

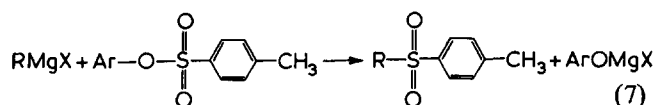
Reaction of equimolar quantities of α -methylstyrene and phenyl bromide with lithium metal in THF yielded a product which was precipitable from methanol, and was shown by ^1H n.m.r. to be poly(α -methylstyrene). G.l.c. analysis of the reaction mixture showed that very little (<5%) of the monomer appeared as the dimer diadduct II, and that the phenyl bromide had been virtually completely converted to biphenyl (Table I). Again, an argument similar to that employed with ethyl tosylate may be used to explain these results. The polarizability of the aromatic ring allows the halide to compete with the monomer for reactive sites on the metal surface, where it is converted to phenyl lithium, and this reagent then couples with a phenyl bromide molecule adsorbed in an adjacent position. It is interesting to note that under these experimental conditions the phenyl moiety appears in the product almost exclusively as biphenyl, whereas in the homogeneous reaction with the tetramer it appears almost exclusively as benzene. Since it is unlikely that the difference in Gegen ion in these two experiments could make such a dramatic difference in the behaviour of the phenyl anion, it must be concluded that the condensation reaction between the two adsorbed species involves a lower activation energy, and therefore takes place much more rapidly than the same reaction in bulk.

The reaction of phenyl tosylate with the α -methylstyrene tetramer in THF resulted in the formation of a white precipitate with a yellow coloured supernatant liquid which was decolourized by addition of water. The filtrate was shown to contain α -methylstyrene oligomers with an average molecular weight (polystyrene equivalent) of about 2000, and this accounted for virtually all the tetramer originally present. The hydrolysed THF solution also contained phenol, presumably derived from the tosylate. The precipitate was approximately equal in weight to the phenyl tosylate added, and consisted of various components since 40% could be subsequently dissolved in THF, 55% was soluble in water and 5% was soluble in neither. This precipitated material was derived principally from the phenyl tosylate and, as the investigation was primarily to examine the effect of phenyl tosylate on the tetramer, it was not examined further.

The presence of phenol in the product is of significance since it shows that nucleophilic attack does not occur at the carbon-oxygen bond as with the alkyl tosylates (equation 6), but as the adjacent oxygen-sulphur bond.

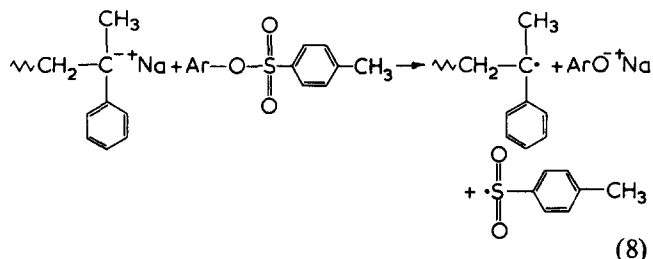


The susceptibility of aromatic tosylates to attack at this point is supported by their reaction with Grignard compounds to form sulphones in appreciable yields⁹ (equation 7).



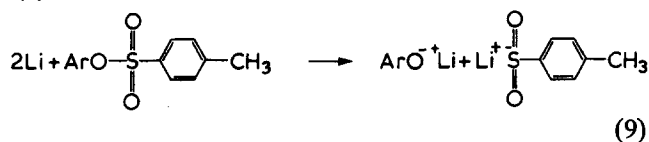
Although this reaction explains the observed phenol in the reaction products, it does not explain the formation of oligomeric α -methylstyrene, nor the separation by precipitation of the tosylate residues. The authors suggest that steric factors prevent the α -methylstyryl anion reacting as in

equation (7) to form the sulphone adduct, and that an electron transfer reaction occurs as illustrated in equation (8)



to produce an α -methylstyryl radical which can then terminate bimolecularly by combination to produce the α -methylstyrene oligomers observed. A similar mechanism was proposed for the reaction of the tetramer with sterically hindered alkylhalides¹⁷. The sulphonyl radical generated may react in a variety of ways to produce the multicomponent precipitate observed in the reaction.

In the reaction of equimolar phenyl tosylate and α -methylstyrene with lithium in THF, the solution took on a yellow hue, stable at room temperature, but discharged by adding water. A small amount of low molecular weight poly(α -methylstyrene) was precipitated on addition of the solution to methanol, and g.l.c. analysis of the volatile products showed them to consist of hydrogen terminated oligomers of α -methylstyrene up to tetramer (40%), phenol (20%) and unreacted phenyl tosylate (50%). At least part of the phenol could have been produced by direct reaction of phenyl tosylate with the metal, as there was a considerable amount of pitting on the surface (reaction with monomer results in the metal retaining its initial smooth surface). This was confirmed by allowing phenyl tosylate to react in THF with lithium metal in the absence of monomer for 24 h, when again extensive pitting was observed and the hydrolysed product showed 92% conversion to phenol. The reaction taking place is almost certainly as shown in equation (9).



The presence of hydrogen-terminated oligomers and only a comparatively small amount of precipitated poly(α -methylstyrene) must be commented upon. Firstly, the reaction of the α -methylstyryl anion with phenyl tosylate (equation 8) is likely to be significantly slower than the more normal metathetical reaction (equation 6), so that the dimer dianion generated at the surface is more likely to propagate before termination. Secondly, because the dimer dianions are being generated slowly over a total reaction time of about three hours, the radical concentration resulting from the electron transfer process is very low, in contrast to that generated by the rapid reaction of phenyl tosylate with tetramer. This means that the kinetic lifetime of the radicals is long and this promotes their termination by hydrogen abstraction from solvent rather than by bimolecular termination. The former point explains the presence of excess phenyl tosylate in the reaction product whilst the latter explains the presence of hydrogen-terminated oligomers and the low yield of polymeric material.

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