

## Michael Reactions Catalysed by Polymer-supported Quaternary Ammonium Salts Derived from Cinchona and Ephedra Alkaloids

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Reaction of chloromethylated crosslinked polystyrenes with cinchonidine, cinchonine, or (–)-*N*-methyl-ephedrine gave polymer-supported chiral quaternary ammonium chlorides. The hydroxide, hydrogen carbonate, fluoride, and chloride forms of these polymers, and also of a commercial polymer containing achiral quaternary ammonium groups, catalyse one or more of the following Michael reactions: (1) The addition of methyl 1-oxoindan-2-carboxylate to methyl vinyl ketone, (2) the addition of ethyl 2-oxocyclohexanecarboxylate to methyl vinyl ketone, and (3) the addition of thio-*p*-cresol to cyclohex-2-enone. Catalysts prepared from cinchonidine achieve optical yields of  $\leq 27\%$  of the *S*-adduct from reaction (1), whilst those catalysts prepared from cinchonine achieve optical yields of  $\leq 13\%$  of the *R*-adduct. This is one of the few instances where the use of polymer-supported chiral quaternary ammonium salts has given substantial optical yields. With reactions (2) and (3) the optical yields were all  $< 2.5\%$ . The catalysts are chemically fragile but, at least with reaction (1), can be re-used several times.

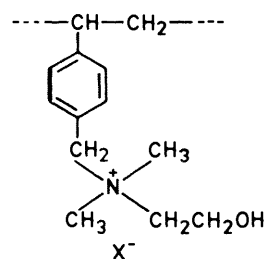
Polymer-supported quaternary ammonium hydroxides have been used to catalyse Michael reactions.<sup>1</sup> Attractive features of such catalysts are that they are easily removed at the end of the reaction and can possibly be re-used.<sup>2</sup> We have investigated the catalysis of reactions (1)–(3) by various polymer-supported quaternary ammonium salts derived from cinchona or ephedra alkaloids. In many cases the products were optically active. Closely related derivatives of some of the polymers we studied have previously been used as phase-transfer catalysts for addition reactions.<sup>3,4</sup>

**Catalysis of Reaction (1).**—To determine which anionic forms of polymer-supported quaternary ammonium salts could serve as catalysts, polymers (I)–(III) were prepared by standard methods from a commercial resin containing residues (IV). This resin was selected because the catalysts to be prepared using the alkaloids would also contain a hydroxy group *beta* to the quaternary centre.

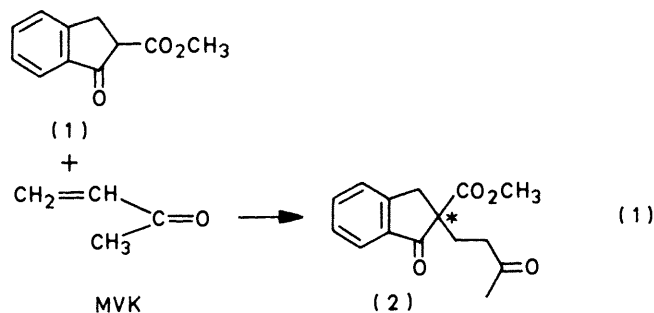
Samples of polymers (I)–(IV) were separately stirred with mixtures of methyl 1-oxoindan-2-carboxylate (1) and methyl vinyl ketone (MVK) in toluene at 20 °C. All four polymers catalysed the reaction (see Table 1, entries 2–5): no reaction occurred if the polymer was simply an unsubstituted crosslinked polystyrene. Hydroxide and fluoride forms of anion-exchange resins are known to catalyse other Michael reactions,<sup>1,5</sup> but polymer (II) appears to be the first example of a hydrogencarbonate form serving as a catalyst. Although the chloride form was substantially less active than the others, the fact it catalysed the reaction at all is surprising. It may operate like the fluoride form,<sup>5</sup> albeit less efficiently, by hydrogen-bonding to the acidic hydrogen atom in the substrate.

A range of catalysts were prepared from cinchonidine (see Table 2). Chloromethylation of a 2% crosslinked polystyrene and reaction of the product with cinchonidine gave polymer (V).<sup>3</sup> The hydroxide form (VI) and hydrogencarbonate form (VII) were prepared by ion exchange, and treatment of the latter with hydrofluoric acid gave the fluoride form (VIII), in which the quinoline moiety was present as the hydrofluoride. Catalysts (IX)–(XII) were prepared similarly from a 20% crosslinked macroporous polystyrene.

Catalytic amounts of polymers (V)–(XII) were stirred with the indanone (1) and MVK in toluene or carbon tetrachloride at 20 °C. Although the reactions were slow under these conditions it was expected that higher reaction temperatures would result in lower optical yields. The following conclusions



- (I)  $X^- = OH^-$   
 (II)  $X^- = HCO_3^-$   
 (III)  $X^- = F^-$   
 (IV)  $X^- = Cl^-$



can be drawn from the experiments summarised in Table 1, entries 6–14. First, all the polymers functioned as catalysts, the most active being the hydroxide and hydrogencarbonate forms. Secondly, the products were optically active, the (–)-isomer of compound (2) being the major product. Thirdly, in most cases the 20% crosslinked macroporous polymers gave better optical yields than the corresponding 2% crosslinked polymers. Finally, for a given anion the better optical yields were in the range 22–27%.

Reaction of the chloromethylated 20% crosslinked macroporous polystyrene with cinchonine gave polymer (XIII), and this was converted by ion exchange into polymer (XIV) (see Table 2). Both these polymers catalysed reaction 1 (see Table 1, entries 15–17), the hydrogencarbonate form being better

**Table 1.** Reaction of the indanone (1) with methyl vinyl ketone in the presence of various polymer-supported catalysts <sup>a</sup>

Entry	Catalyst <sup>*</sup>	Reaction solvent <sup>b</sup>	Reaction time (h)	Chemical yield (%) <sup>c</sup>	Optical yield (%) <sup>d</sup>	Configuration of major product
1	Polystyrene <sup>e</sup>	A	72	0	—	—
2	(I)	A	72	92	—	—
3	(II)	A	72	100	—	—
4	(III)	A	72	100	—	—
5	(IV)	A	72	20	—	—
6	(V)	A	240	33	19	<i>S</i>
7	(VI)	A	240	82	25	<i>S</i>
8	(VII)	A	240	70	13	<i>S</i>
9	(VIII)	A	360	77	5	<i>S</i>
10	(IX)	A	240	66	23	<i>S</i>
11	(X)	A	120	71	7	<i>S</i>
12	(XI)	A	120	100	22	<i>S</i>
13	(XI)	B	120	100	15	<i>S</i>
14	(XII)	A	240	61	27	<i>S</i>
15	(XIII)	A	240	30	8	<i>R</i>
16	(XIV)	A	120	94	13	<i>R</i>
17	(XIV)	B	120	85	10	<i>R</i>
18	(XV)	A	360	30	0	—

<sup>a</sup> See Experimental section for full details of typical reactions. <sup>b</sup> A = Toluene, B = CCl<sub>4</sub>. <sup>c</sup> Average of two or more runs. <sup>d</sup> Average of two or more runs which were within  $\pm 1\%$  of values given. <sup>e</sup> 2 or 20% Crosslinked polystyrene.

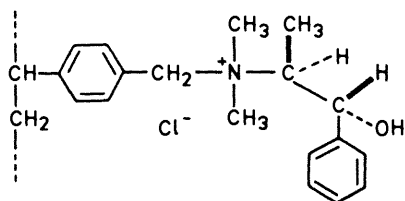
<sup>\*</sup> Catalysts (V)–(XIV) given in Table 2. Catalyst (XV) given in text.

**Table 2.** Structures and capacities of catalysts derived from cinchona alkaloids

(V)–(XIV)

Catalyst	Crosslinking of polymer (%)	Configuration		X <sup>-</sup>	Amount of X <sup>-</sup> present (mmol per g)
		C-8	C-9		
(V)	2	<i>S</i>	<i>R</i>	Cl <sup>-</sup>	1.92
(VI)	2	<i>S</i>	<i>R</i>	OH <sup>-</sup>	1.44
(VII)	2	<i>S</i>	<i>R</i>	HCO <sub>3</sub> <sup>-</sup>	1.29
(VIII)	2	<i>S</i>	<i>R</i>	F <sup>-</sup>	1.31 *
(IX)	20	<i>S</i>	<i>R</i>	Cl <sup>-</sup>	0.73
(X)	20	<i>S</i>	<i>R</i>	OH <sup>-</sup>	0.69
(XI)	20	<i>S</i>	<i>R</i>	HCO <sub>3</sub> <sup>-</sup>	0.50
(XII)	20	<i>S</i>	<i>R</i>	F <sup>-</sup>	0.52 *
(XIII)	20	<i>R</i>	<i>S</i>	Cl <sup>-</sup>	0.65
(XIV)	20	<i>R</i>	<i>S</i>	HCO <sub>3</sub> <sup>-</sup>	0.58

\* In addition, the quinoline moiety was present as the hydrofluoride.



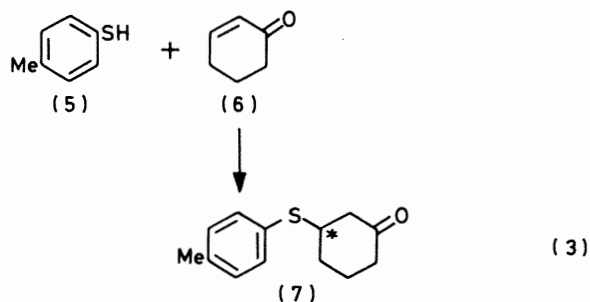
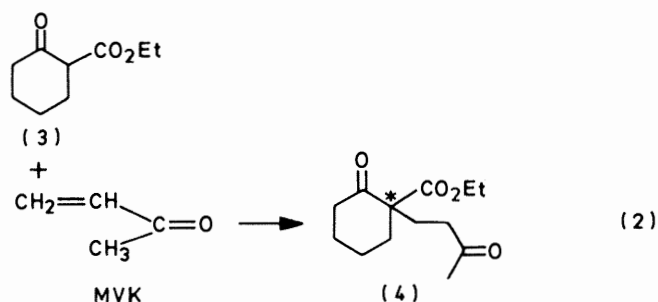
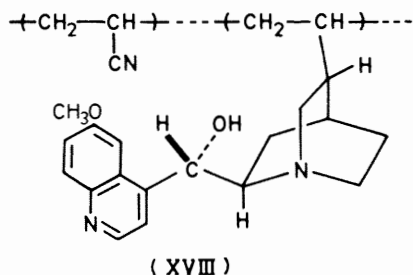
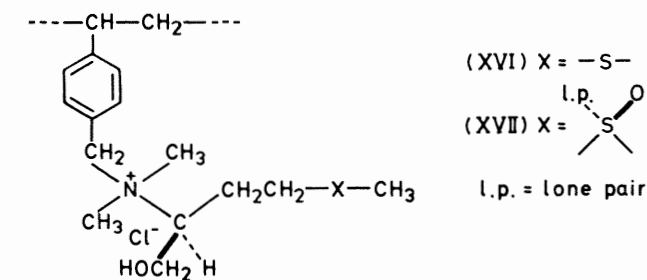
(XV) 20% Crosslinked polymer; 1.34 mmol of Cl<sup>-</sup> per g

than the chloride form. With these catalysts the main product was the (+)-isomer of compound (2). With polymer (XIV), as with polymer (XI) above, the optical yields were somewhat lower when carbon tetrachloride rather than toluene was the reaction solvent.

Finally, polymer (XV) was prepared by treating (–)-*N*-methylephedrine with the chloromethylated 20% crosslinked polystyrene. This catalyst was chemically active (Table 1, entry 18) but the product was optically inactive. No further studies were made.

Our observation that the major products obtained using catalysts derived from cinchonidine have the opposite configuration to the major products obtained using catalysts derived from cinchonine agrees with results obtained in other reaction systems.<sup>6</sup> So too does the fact that the catalyst derived from the *N*-methylephedrine gave a lower optical yield (in this case zero) than the corresponding catalysts derived from the 'more rigid' cinchona alkaloids.<sup>6</sup>

The best optical yields we obtained were 27% for the (–)-isomer and 13% for the (+)-isomer of adduct (2). When polymer-supported chiral quaternary ammonium salts (XVI)



and (XVII) were used to catalyse reaction (1) the optical yields were zero,<sup>7</sup> and when quinine methohydroxide or quinine methiodide (low-molecular-weight compounds closely related to our catalysts) were used, the optical yields of the (-)-isomer were 15 and 12%, respectively.<sup>8</sup> Better optical yields have been obtained using catalysts which do not contain quaternary ammonium groups, for example, the polymer-supported catalyst (XVIII) (optical yields  $\leq 42\%$ )<sup>9</sup> or free cinchona alkaloids ( $\leq 76\%$ ).<sup>8</sup>

Quaternary salts of cinchona alkaloids tend to fragment in the presence of base with cleavage of the C-8-N bond.<sup>10</sup> The stability of two of the present catalysts was, therefore, investigated. Catalyst (X) was re-used once and catalyst (XI) twice with essentially the same results as when they were first used. The recovered catalysts were then stirred with the indanone (1) for a prolonged period before being filtered off and used as before. The optical yields now differed; 12 and 13% for catalysts (X) and (XI), respectively, compared with

7 and 22% originally. More significantly, the filtrates had a low catalytic activity (11% yield of adduct after 5 d). The optical yields were, however, zero. This suggests a different mode of decomposition than cleavage of the C-8-N bond, since the latter would not release base into solution. Neither could it be due to nucleophilic cleavage of the polymer-nitrogen bond, since this would release cinchonidine into solution. This compound can catalyse reaction (1) but it would almost certainly achieve substantial asymmetric synthesis.<sup>8</sup> In summary, it appears that whilst there is some decomposition of the catalysts on repeated use, they can be re-used successfully several times.

**Catalysis of Reaction (2).**—Attempts to extend the work to the catalysis of reaction (2) met with only limited success. When polymers (X) and (XI) [two of the better catalysts for reaction (1)] were used, the reactions were very slow (22 and 38% yield, respectively, after 10 d at 20 °C). The optical yield obtained with catalyst (X) was 2.5%, the (-)-isomer of compound (4) being the major product. With catalyst (XI) the optical yield was zero. These results compare with an optical yield of 22% obtained with quinine methohydroxide.<sup>8</sup>

**Catalysis of Reaction (3).**—This reaction proceeded slowly without any added catalyst and when reactions were carried out in the presence of several of the polymer-supported catalysts (see Table 3) the chemical yields were excellent but the optical yields were very poor ( $< 2\%$ ). As with reaction (1), the major products with the cinchonidine-derived and cinchonine-derived catalysts had opposite configurations. Attempts to obtain better optical yields by drying the catalysts by azeotropic distillation in the presence of the thiol (5) before addition of the enone (6) led to a serious catalyst decomposition. Thus, if the polymer was filtered off, the filtrate catalysed reaction (3) and gave excellent chemical and optical yields. This was not surprising as quaternary ammonium salts undergo nucleophilic substitution by thiols in the presence of base.<sup>11</sup> In the present case this would release cinchonidine or cinchonine into solution and these compounds are known to catalyse reaction (3) and to achieve asymmetric synthesis.<sup>6</sup> Our catalysts did not, however, appear to decompose under the reaction conditions when no attempt was made to dry the catalyst and the reactions were carried out at 20 °C.

**Conclusion.**—The polymer-supported catalysts discussed above give satisfactory results with reaction (1), but not with reactions (2) and (3). This appears to be one of the few occasions<sup>4</sup> that the use of polymer-supported chiral quaternary ammonium salts as catalysts has given substantial optical yields. The catalysts are chemically fragile but, at least with reaction (1), can be re-used several times.

## Experimental

M.p.s were measured with a Kofler hot-stage apparatus. I.r. spectra were measured for KBr discs on a Nicolet MX-1 FT-IR instrument. <sup>1</sup>H N.m.r. spectra were measured for solutions in deuteriochloroform containing tetramethylsilane as internal standard on a Jeol FX-100 instrument operating at 99.55 MHz. Polymer samples were dried to constant weight in a vacuum oven (2 mmHg) at 50 °C. Rotations were determined with a Perkin-Elmer 141 Polarimeter. G.l.c. was carried out with a Pye 104 machine (flame-ionisation detector) and a 5 ft column containing SE30 as stationary phase. Ether refers to diethyl ether.

**Preparation of Catalyst (I).**—Aqueous sodium hydroxide (1M) was passed down a column of the chloride form of

**Table 3.** Reaction of thio-*p*-cresol (5) with cyclohex-2-enone (6) in the presence of various polymers <sup>a</sup>

Entry	Catalyst	Reaction solvent <sup>b</sup>	Reaction time (h)	Chemical yield (%) <sup>c</sup>	Optical yield (%) <sup>c</sup>	Configuration major product
1	—	A	96	55	—	—
2	(VI)	A	72	95	1	R
3	(VII)	A	48	100	1	R
		B	48	93	1	R
4	(XI)	A	24	94	2	R
		B	24	96	1	R
5	(XIV)	A	24	100	2	S

<sup>a</sup> See Experimental section for full details of a typical reaction. <sup>b</sup> A = Toluene, B = CCl<sub>4</sub>. <sup>c</sup> Average of two or more runs.

Amberlite IRA 410 (25.0 g, damp) until the eluate no longer contained chloride ion (test with silver nitrate). The resin was then transferred to a sintered-glass filter and was washed successively with water (2 ×), methanol (2 ×), and ether (2 ×), then dried. By titration against sulphuric acid the product (16.8 g), catalyst (I), contained 3.09 mmol of hydroxide anion per g.

**Preparation of Catalyst (II).**—The chloride form of Amberlite IRA 410 (45.0 g, damp) was stirred with a solution of sodium hydrogencarbonate (45.0 g) in water (400 ml). After 12 h the resin was allowed to settle and the aqueous solution was decanted off. The treatment was repeated. The resin was then filtered off and washed successively with water (3 ×), tetrahydrofuran (THF) (2 ×), and ether (2 ×), then dried. The product (28.7 g), catalyst (II), by titration against hydrochloric acid, contained 2.73 mmol of hydrogencarbonate anion per g.

**Preparation of Catalyst (III).**—Aqueous hydrofluoric acid (2.0 ml; 40% solution) was carefully added to a suspension of the hydrogencarbonate form of Amberlite 410 (14.0 g; 2.73 mmol of hydrogencarbonate per g) in water (80 ml). Carbon dioxide was liberated. The resin was filtered off and successively washed with water (2 ×), acetone (2 ×), and ether (2 ×), then dried. The product (11.6 g), catalyst (III), did not react with acid. On the assumption that no resin was lost, the product was calculated to contain 3.29 mmol of fluoride anion per g.

**Preparation of Catalyst (IV).**—The chloride form of Amberlite IRA 410 (45.0 g, damp) was washed successively on a sintered-glass filter with water (2 ×), THF (2 ×), and ether (2 ×), then dried. The product (28.0 g), catalyst (IV), was found by Volhard titration<sup>12</sup> to contain 3.70 mmol of chloride anion per g.

**Chloromethylation of Polystyrenes.**—The 2% crosslinked polystyrene beads (Biobeads SX2) and the 20% crosslinked macroporous polystyrene beads (Biobeads SM2) were obtained from Biorad Laboratories, Richmond, California. Chloromethylations were carried out as before.<sup>13</sup> The chloromethyl contents of the products were determined by treating samples with pyridine,<sup>14</sup> then estimating the chloride ion produced by Volhard titrations.<sup>12</sup> The 2 and 20% crosslinked products contained, respectively, 4.85 and 2.48 mmol of chloromethyl groups per g, corresponding to degrees of functionalisation of 0.66 and 0.29.

**Preparation of Catalysts (V), (IX), (XIII), and (XV) and Their Derivatives.**—The following is typical of the procedure used to prepare these catalysts and their derivatives. The capacities of the products are summarised in Table 2. Cinchonidine, cinchonine, and (–)-*N*-methylephedrine were obtained from Aldrich.

**Preparation of catalyst (V) and its derivatives.** A mixture of the above chloromethylated 20% crosslinked polystyrene (18.66 g) and cinchonidine (30.11 g) in *NN*-dimethylformamide (100 ml) was stirred at 100 °C under nitrogen for 45 h. The mixture was then cooled and the polymer was filtered off and washed thoroughly and successively with chloroform (4 ×), methylene dichloride (2 ×), and ether (2 ×), then dried. The product (23.9 g), catalyst (V), contained, by Volhard titrations,<sup>12</sup> 0.73 mmol of chloride anion per g, corresponding to a reaction yield of 38% and a degree of functionalisation by residues (V) of 0.11.

The product was converted into the other anionic forms (VI)—(VIII) using procedures similar to those described above. Note that the quinoline moiety reacts with the strong acids used in the titrations.

**Reactions Summarised in Table 1.**—The following reactions are typical.

**Entry 7.** A mixture of methyl 1-oxoindan-2-carboxylate (1)<sup>15</sup> (229 mg, 1.31 mmol), catalyst (VI) (48 mg; 0.07 mmol of hydroxide), and MVK (87.5 mg, 1.25 mmol) in dry toluene (5 ml) was stirred under nitrogen for 10 d. The polymer was then filtered off and washed with toluene (20 ml). The combined toluene extracts were washed successively with 2M hydrochloric acid (2 × 20 ml), 2M aqueous potassium hydroxide (2 × 10 ml), and brine (2 × 20 ml), then dried (MgSO<sub>4</sub>). Evaporation of the solvent gave the adduct (2) (273 mg, 89%) as a clear oil which crystallised with time. It had m.p. 95–98 °C (lit.,<sup>16</sup> 104–106 °C);  $\nu_{\max}$  1733 (ester carbonyl) and 1717 and 1711 cm<sup>-1</sup> (ketone carbonyls);  $\delta$  2.13 (3 H, s, acetyl), 2.26 (2 H, m, side-chain methylene), 2.54 (2 H, m, side-chain methylene), 3.01 (1 H, d, *J* 17 Hz, 3-H), 3.68 (3 H, s, OCH<sub>3</sub>), 3.70 (1 H, d, *J* 17 Hz, 3-H), and 7.2–8.0 (4 H, m, ArH). The product had  $[\alpha]_{578}^{19} - 19.5^\circ$  (*c* 2 in benzene) {lit.,<sup>8,16</sup> enantiomerically pure *S*-isomer has  $[\alpha]_{578}^{RT} - 77^\circ$  (*c* 2 in benzene)} corresponding to an optical yield of 25%.

A duplicate experiment afforded adduct (2) in 75% yield with  $[\alpha]_{578}^{19} - 18.5^\circ$  (*c* 2 in benzene) corresponding to an optical yield of 24%.

**Entry 16.** A similar experiment was carried out using the indanone (1) (457 mg, 2.62 mmol), catalyst (XIV) (237 mg; 0.14 mmol of hydrogencarbonate), and MVK (175 mg, 2.50 mmol) in toluene (10 ml). After 5 d the yield of adduct (2) was 87%. It had  $[\alpha]_{578}^{19} + 10.3^\circ$  (*c* 2 in benzene) corresponding to an optical yield of 13%.

A duplicate experiment afforded adduct (2) in 100% yield with  $[\alpha]_{578}^{19} + 9.5^\circ$  (*c* 2 in benzene) corresponding to an optical yield of 12%.

**Stability of Catalysts (X) and (XI).**—After catalyst (X) (200 mg) had been used to carry out the reaction summarised in Table 1, entry 11, it was recovered and re-used. On this occasion the chemical yield was 69%, and the optical yield was 7%. Catalyst (X) was recovered again and was then stirred

with a solution of the indanone (1) (450 mg) in toluene (10 ml) for 240 h at 20 °C. The catalyst was filtered off and the filtrate was stored. The catalyst was then used to catalyse reaction (1) a third time. On this occasion the chemical yield was 59% after 120 h and the optical yield 12%. Indanone (1) and MVK were added to the above filtrate. After 120 h the yield of adduct (2) was 11%; the product was optically inactive.

After it had been used to catalyse the experiment summarised in Table 1, entry 12, catalyst (XI) was re-used twice. On these occasions the chemical yields were 98 and 92%, respectively, and the optical yields were 21 and 20%. After being stirred with the indanone (1), as above, using the polymer as a catalyst for the fourth time gave a 66% yield of adduct (2) after 120 h; the optical yield was 13%. Using the filtrate as a catalyst afforded, after 120 h, an 11% yield of adduct (2) which was optically inactive.

**Reaction (2).**—The following experiment is typical. Results from the other experiments are given in the text.

Ethyl 2-oxocyclohexanecarboxylate (3) (224 mg, 1.31 mmol), catalyst (X) (100 mg, 0.07 mmol), and MVK (90 mg, 1.25 mmol) in toluene (5 ml) were stirred at 20 °C under nitrogen for 240 h. The product was isolated using the usual procedure. The adduct (4) (65 mg, 22% yield) was obtained as a clear oil with  $v_{\max}$  (liquid film) 1740 (ester) and 1716  $\text{cm}^{-1}$  (ketone);  $\delta$  1.28 (3 H, t,  $J$  7 Hz,  $\text{CH}_3\text{CH}_2\text{O}$ ), 1.5—2.8 (12 H, m,  $6 \times \text{CH}_2$ ), 2.16 (3 H, s, acetyl), and 4.26 (2 H, q,  $J$  7 Hz,  $\text{CH}_3\text{CH}_2\text{O}$ ). These spectra were identical with those of an authentic sample<sup>17</sup> and both samples were pure by g.l.c. (SE30 column at 200 °C). The reaction product had  $[\alpha]_{578}^{19} + 2.1^\circ$  ( $c$  2.5 in carbon tetrachloride) {lit.,<sup>8</sup> calculated for enantiomerically pure *R*-isomer:  $[\alpha]_{578}^{\text{RT}} + 81^\circ$  ( $c$  2 in carbon tetrachloride)} corresponding to an optical yield of 2.6%.

A duplicate experiment gave the adduct (4) in 25% yield with  $[\alpha]_{578}^{19} + 2.0^\circ$  ( $c$  2.5 in carbon tetrachloride) corresponding to an optical yield of 2.5%.

**Reactions Summarised in Table 2.**—The following reaction is typical.

**Entry 4.** A mixture of thio-*p*-cresol (5) (587 mg, 4.7 mmol), cyclohex-2-enone (6) (432 mg, 4.5 mmol), and catalyst (XI) (450 mg; 0.23 mmol of hydrogencarbonate) in toluene (10 ml) was stirred at 20 °C under nitrogen for 24 h. The polymer was then filtered off and the filtrate was diluted with toluene (10 ml). The toluene solution was washed successively with 2M hydrochloric acid ( $2 \times 10$  ml), 2M aqueous potassium hydroxide ( $2 \times 10$  ml), and brine ( $2 \times 10$  ml) and was dried ( $\text{MgSO}_4$ ). Evaporation of the solvent left adduct (7) as an oil (1.0 g, 92% yield), b.p. 150 °C at 0.06 mmHg (lit.,<sup>18</sup> 147—149 °C at 0.07 mmHg);  $v_{\max}$  (liquid film) 1715  $\text{cm}^{-1}$ ;  $\delta$  1.5—3.0 (8 H, m,  $4 \times \text{CH}_2$ ), 2.24 (3 H, s,  $\text{ArCH}_3$ ), 3.35 (1 H, m, CHS), and 7.0—7.5 (4 H, m, ArH);  $[\alpha]_{578}^{18} + 1.1^\circ$  ( $c$  1 in benzene) {lit.,<sup>6,18</sup> for optically pure *R*-isomer:  $[\alpha]_{578}^{21} + 70^\circ$  ( $c$  in benzene)} corresponding to an optical yield of 1.6%.

A duplicate experiment gave adduct (7) in 95% yield with  $[\alpha]_{578}^{18} + 1.2^\circ$  ( $c$  1 in benzene) corresponding to an optical yield of 1.7%.

**Stability of Catalyst (VII) to Thio-*p*-cresol.**—A mixture of catalyst (VII) (178 mg; 0.23 mmol of hydrogencarbonate) and thio-*p*-cresol (578 mg, 4.7 mmol) in toluene (10 ml) was dried by azeotropic distillation during 3 h. The polymer was then filtered off and the filtrate was stored. The polymer was used to catalyse a reaction between thio-*p*-cresol (5) and cyclohex-2-enone (6) in toluene at 20 °C in the usual way. After 48 h the yield of adduct (7) was 100% and it had  $[\alpha]_{578}^{20} + 15.4^\circ$  ( $c$  1 in benzene) corresponding to an optical yield of 22%. The above filtrate and cyclohex-2-enone (432 mg, 4.5 mmol) were stirred together at 20 °C for 48 h. The yield of adduct (7) was 100% and it had  $[\alpha]_{578}^{20} + 40.5^\circ$  ( $c$  1 in benzene) corresponding to an optical yield of 58%.

When the above experiment was repeated but the initial mixture not heated, the filtrate did not catalyse reaction (3).

### Acknowledgements

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