

## The use of polymer supports in organic synthesis. XII. The total stereoselective synthesis of *cis* insect sex attractants on solid phases

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THOMAS M. FYLES, CLIFFORD C. LEZNOFF, and JOHN WEATHERSTON. Can. J. Chem. 55, 4135 (1977).

A 2% crosslinked divinylbenzene-styrene copolymer, incorporating trityl chloride groups (2) was used in the synthesis of insect sex attractants of Lepidoptera by a two-step alkyne coupling route. Polymer 2 reacted with the symmetrical diols, 1,8-octanediol and 1,10-decanediol, to give the monoblocked polymer-bound diols 5 and 6 respectively. Mesylation of 5 and 6 gave the polymer-bound monomesylates 7 and 8 which on coupling with lithioacetylide gave the polymer-bound terminal alkynes 9 and 10 respectively. Acid cleavage of 9 and 10 provide 9-decyn-1-ol and 11-dodecyn-1-ol respectively. A second coupling step was performed by lithiation of 9 and 10 with *n*-butyllithium or *tert*-butyllithium followed by treatment with *n*-butyl bromide or ethyl bromide to give polymer-bound internal alkynes, which on acid hydrolysis gave 9-tetradecyn-1-ol (22), 11-hexadecyn-1-ol (23), and 11-tetradecyn-1-ol (24). If 10 had been lithiated with *n*-butyllithium and coupled with ethyl bromide, some translithiation occurred to liberate *n*-butyl bromide which entered into the coupling reaction eventually giving a mixture of 23 and 24. This problem was resolved by the use of *tert*-butyllithium in the lithiation step. Attempts were made to reduce polymer-bound internal alkynes stereoselectively to *cis*-alkenes with 9-borabicyclononane, diisobutylaluminum hydride, and catechol borane but all these reagents proved inadequate due to incomplete reduction, overreduction, hydrogenolysis of the alkyne from the polymer, and non-selectivity. Polymer-bound internal alkynes were quantitatively reduced exclusively to *cis* insect sex attractants using disiamylborane without concurrent overreduction or hydrogenolysis.

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On a utilisé un copolymère divinylbenzène-styrène réticulé à 2% et incorporant des groupes chlorure de trityle (2) pour réaliser la synthèse de l'attirant sexuel de Lepidoptera en faisant appel à un schéma de couplage d'alcynes impliquant deux étapes. Le polymère 2 réagit avec les diols symétriques octanediol-1,8 et décanediol-1,10 pour conduire suivant le cas aux diols monobloqués 5 et 6 liés au polymère. La méthylation de 5 et 6 fournit les monomésylates 7 et 8 liés au polymère qui, par couplage avec l'acétylure de lithium, conduisent respectivement aux alcynes terminales 9 et 10 liés au polymère. Une scission acide de 9 et 10 conduit respectivement aux décyn-9 ol-1 et dodécyn-11 ol-1. Une nouvelle étape de couplage, effectuée par la lithiation de 9 et 10 avec le *n*-butyllithium ou le *tert*-butyllithium, suivie par un traitement avec le bromure de *n*-butyle ou le bromure d'éthyle conduit aux alcynes internes liés au polymère qui par hydrolyse acide fournissent le tétradécyn-9 ol-1 (22), l'hexadécyn-11 ol-1 (23) et le tétradécyn-11 ol-1 (24). Si l'on avait effectué la lithiation de 10 avec du *n*-butyllithium et si on l'avait couplé avec du bromure d'éthyle, il se serait produit un peu de translithiation pour libérer du bromure de *n*-butyle qui peut entrer éventuellement dans la réaction du couplage pour conduire à un mélange de 23 et de 24. On a résolu ce problème par l'utilisation du *tert*-butyllithium dans l'étape de lithiation. On a effectué des essais pour réduire d'une façon stéréosélective les alcynes internes liés au polymère afin d'obtenir des alcènes *cis*; à cette fin on a fait appel au 9-borabicyclononane, à l'hydruure de diisobutylaluminium et au catéchol-borane mais tous ces réactifs s'avèrent inadéquats à cause soit d'une réduction incomplète, d'une réduction trop grande, d'une hydrogénolyse de l'alkyne du polymère ou à cause de la non-sélectivité. On a pu réduire quantitativement les alcynes internes liés au polymère et obtenir exclusivement les attractants sexuels des insectes *cis* en faisant appel au disiamylborane sans obtenir de réduction supplémentaire ou d'hydrogénolyse.

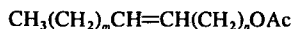
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## Introduction

Recently, we have reported the preparation of insect sex attractants (shown below) of Lepidop-



*cis*

where  $m = 1-3$  and  $n = 6, 8-10$

tera on solid phases by an alkyne coupling route and by two different Wittig sequences (1, 2). The yields of reactions on solid phases, the use of symmetrical starting materials (3), the simplicity of solid phase reactions (4, 5), and the potential for synthesis in an automated procedure (6) showed distinct promise over solution phase methods, but several problems remained to be solved for the complete stereoselective synthesis of insect sex attractants (7) on solid phases. The use of expensive terminal alkynes in the coupling step can be construed as a disadvantage in both solid phase and solution methods of synthesis. Furthermore, in our previous syntheses on solid phases via the alkyne coupling route, the polymer-bound alkyne was cleaved from the polymer before stereoselective reduction to *cis* insect sex attractants was attempted. The stereoselective reduction was then achieved using 9-borabicyclonane (9-BBN) in solution (2, 8). A complete solid phase synthesis of *cis* insect sex attractants would require that the stereoselective *cis* reduction of an internal alkyne be accomplished directly on the polymer support. In this report we describe the synthesis of insect sex attractants on solid phases by a two-step alkyne coupling route using only acetylene and alkyl halides (9, 10). In addition, the stereoselective reduction of a polymer-bound alkyne to a polymer-bound *cis*-alkene by an examination of a variety of soluble reducing agents is described.

## Results and Discussion

### *The Two-step Alkyne Route*

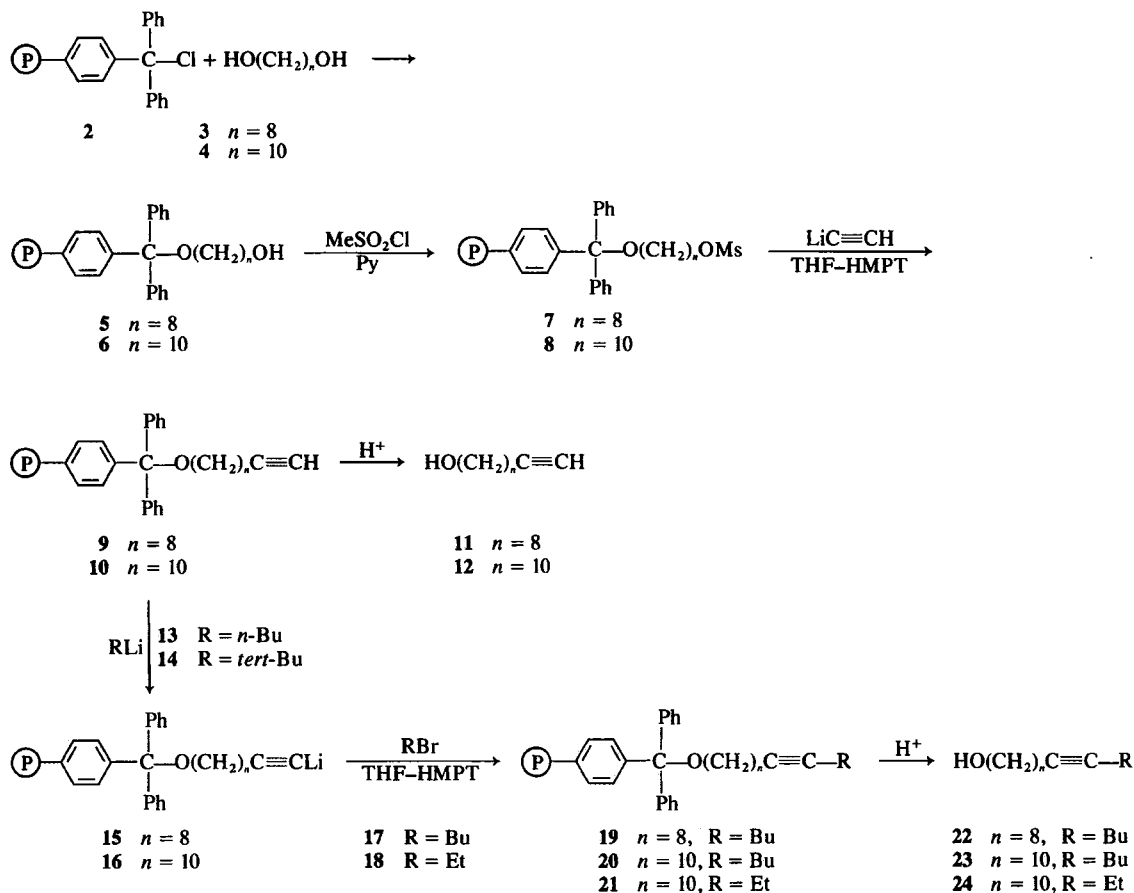
A 2% crosslinked divinylbenzene (DVB)-styrene copolymer, incorporating trityl alcohol functional groups (1) (11, 12), was prepared by our direct lithiation method (12) and converted to a polymer-bound trityl chloride (2) (11, 12). Polymer 2 was treated with 1,8-octanediol (3) and 1,10-decanediol (4) for 48 h in pyridine at room temperature to give the monoprotected polymer-bound diols 5 and 6 respectively. Mesylation of 5 and 6 in benzene-pyridine (3:1) gave the polymer-bound symmetrical diol mono-

mesylates 7 and 8 respectively. The amounts of diols bound to 5 and 6 and the yields of monomesylates derived from 7 and 8 were determined by acid cleavage as previously described (2) and are recorded in Table 1.

Monolithioacetylide can now be readily prepared in large quantities (13). Treatment of 7 and 8 with monolithioacetylide in tetrahydrofuran-hexamethylphosphoric triamide (THF-HMPT) (14) gave the polymer-bound terminal alkynes 9 and 10 respectively. Cleavage of 9 and 10 with HCl in dioxane as usual (2) gave 9-decyn-1-ol (11) and 11-dodecyn-1-ol (12) respectively in high conversion (Table 1) and some recovered 3 and 4 respectively. Lithiation of 9 with *n*-butyllithium (13) and 10 with 13 or *tert*-butyllithium (14) yielded the polymer-bound lithioalkynes 15 and 16 respectively. Coupling in THF-HMPT (14) of 15 with *n*-butyl bromide (17) and 16 with 17 or ethyl bromide (18) yielded the polymer-bound alkynes 19-21 respectively as shown in Scheme 1. Polymer-bound alkynes 19 and 21 had been previously prepared by a one-step alkyne coupling route from 7 and 1-lithio-1-hexyne and from 8 using 1-lithio-1-butyne respectively. Acid cleavage of 19-21 gave 9-tetradecyn-1-ol (22), 11-hexadecyn-1-ol (23), and 11-tetradecyn-1-ol (24) in high conversion from the symmetrical diols 3 and 4 (Table 1). All yields in Table 1 are calculated on products purified by preparative thin layer chromatography (tlc).

When a terminal alkyne is lithiated in a normal solution reaction (9, 10), equivalent amounts of *n*-butyllithium can be used to effect the lithiation. On polymer supports it is usually necessary to use excess reagents to drive reactions to completion and hence in our experiments on polymer 10, excess 13 was used. Thus, in the coupling reaction of 16 with ethyl bromide (18), some excess 13 was present, which could and did exchange with 18 to give ethyllithium and some *n*-butyl bromide (17). The coupling of 16 prepared from *n*-butyllithium (13) with 18 thus led to a mixture of 20 and 21, which on acid cleavage gave a mixture of the alkynols 23 and 24. Analysis of this mixture, as their acetates, by high pressure liquid chromatography (hplc) showed that 24 was contaminated by about 15% of 23 (Table 2). The problem of translithiation was overcome by using *tert*-butyllithium (14) for the lithiation step and 24 could be prepared free of 23 (Table 2).

Conditions necessary for the conversion of 9



SCHEME I

and 10 to 22–24 according to Scheme 1 could be readily monitored by hplc analysis of crude 22–24 prepared via solid phases. In practice, the alkyne fraction, containing internal and sometimes terminal alkyne, was separated by preparative tlc from recovered diol and the alkyne fraction and converted to their acetates which were analyzed by hplc. By this method, the amounts of terminal alkyne in 22–24 could be accurately determined (Table 2).

#### *cis* Reductions of Polymer-bound Alkynes

Although we had previously reduced internal alkynes to *cis*-alkenes in solution by catalytic hydrogenation over a Lindlar-type catalyst (2), the results were not completely stereoselective in that less than 85% of the pure *cis* isomers were produced. In addition, the use of an insoluble palladium oxide catalyst would be incompatible with insoluble polymer supports in any attempt

to reduce polymer-bound alkynes to *cis*-alkenes. It had been shown (2, 8) that internal alkynes can be reduced stereoselectively to *cis*-alkenes with soluble 9-BBN. After experimenting with a variety of soluble reducing agents (see below), disiamylborane (15) was found to be ideal for the job of reducing polymer-bound alkynes stereoselectively to polymer-bound *cis*-alkenes. Thus, the polymer-bound internal alkynes, 19 and 21, that had been prepared, in fact, by the one-step alkyne coupling route (2), were treated with a large excess of 0.5 M disiamylborane ((Sia)<sub>2</sub>BH) in THF at 0°C for 4 h. Protonolysis with acetic acid yielded the polymer-bound *cis*-alkenes 25 and 26, which on acid cleavage and acetylation yielded, according to Scheme 2, *cis*-9-tetradecen-1-yl acetate (27) (10), the sex attractant of *Spodoptera frugiperda* (J. E. Smith), and *cis*-11-tetradecen-1-yl acetate (28) (16), the sex attractant of *Argyrotaenia velutinana* (Walker), in high

TABLE 1. Yields of alkynols and intermediates prepared on solid phases via the two-step alkyne route

Internal alkynol	Quantity of diol initially bound to polymers 5 and 6 <sup>a</sup> (mmol/g)	Quantity of diol monomesylate bound to polymers 7 and 8 <sup>b</sup> (mmol/g)	Quantity of terminal alkynol bound to polymers 9 and 10 <sup>c</sup> (mmol/g)	Quantity of recovered diol <sup>d</sup> (mmol/g)	Quantity of internal alkynol bound to polymers 19-21 <sup>e</sup> (mmol/g)	Quantity of recovered diol <sup>f</sup> (mmol/g)	Overall yield of internal alkynols (%)	Overall conversion to internal alkynols <sup>g</sup> (%)
22	0.58	0.29	0.22	0.30	0.21	0.29	36 <sup>h</sup>	73
23	0.69	0.35	0.30	0.35	0.29	0.34	42	83
24	0.69	0.35	0.30	0.35	0.28	0.31	41 <sup>i</sup>	74

<sup>a</sup> Determined by acid cleavage of 5 and 6.

<sup>b</sup> Determined by acid cleavage of 7 and 8.

<sup>c</sup> Determined by acid cleavage of 9 and 10.

<sup>d</sup> Yield determined by acid cleavage of 19-21.

<sup>e</sup> Yield of diol recovered from acid cleavage of 19-21 is recycled.

<sup>f</sup> Solution yield from ref. 10 is 36% based on 8-chloro-1-octanol.

<sup>g</sup> Prepared using 14 as the liberating agent (Scheme 1).

conversion (Table 3). Attractants **27** and **28** were examined by hplc and vapour phase chromatography (vpc) for isomeric purity about the double bond and were found to have *cis:trans* ratios of 99:1 and 90:10 respectively (Table 4).

Earlier attempts to reduce **21** to **26** using excess 9-BBN at 50°C gave complete reduction but some hydrogenolysis (cleavage from the polymer) occurred and the reduction was *not* completely stereoselective even though it was completely stereoselective in solution (Tables 3 and 4). Less vigorous conditions resulted in incomplete reduction of the alkyne (Table 4). Catechol borane (17) has been recently recommended for the stereoselective reduction of alkynes to *cis*-alkenes in solution, but treatment of **21** with catechol borane in dioxane under normal conditions (17) led to complete hydrogenation and hydrogenolysis to 1-tetradecanol, analyzed by hplc as its acetate (Table 4). In THF under reflux, however, only partial reduction of **21** to **26** occurred. In addition, some hydrogenolysis from the polymer took place and product **26** exhibited a *cis:trans* ratio of only 2:3 and hence reduction took place in a non-stereoselective manner (Tables 3 and 4). Diisobutylaluminum hydride (DIBAH) has been used for the stereoselective *cis* reduction of alkynes (18). Treatment of **21** in THF with a slight excess of 1 M DIBAH in hexane at room temperature overnight gave little reaction. With excess DIBAH at 60°C reduction to alkene was still incomplete. Under reflux conditions in benzene, reduction was complete, but hydrogenolysis from the polymer was also complete (Tables 3 and 4). In addition, some 1-tetradecanol, analyzed as its acetate was detected in the filtrate of the polymer, showing that overreduction had occurred. The reductions were not completely stereospecific in that **28** exhibited a *cis:trans* ratio of 85:15.

As shown in Table 3 the stereoselective reductions of **19** and **21** leading to **27** and **28** using (Sia)<sub>2</sub>BH are virtually quantitative. The analogous reaction in solution described by Holan and O'Keefe (15) proceeded very well in 90% yield but was not quite as good as described herein. We have noticed this phenomenon before in which polymer-bound reactions appear to be consistently 5-20% better than their solution analogs (2) although documentation and strict comparisons are difficult to make as, by their very nature, polymer-bound reactions are not

TABLE 2. High pressure liquid chromatographic analysis of the alkynol fractions,<sup>a</sup> obtained under a variety of conditions via **9** and **10** according to Scheme 1

Polymer bound terminal alkyne	Lithiation agent <sup>b</sup>	Alkylating agent <sup>c</sup>	T (°C)	Relative yield of terminal alkynol <sup>a</sup> (%)	Relative yield of internal alkynol <sup>a</sup> (%)	Solvent for hplc analysis <sup>d</sup>
<b>9</b>	<b>13</b>	<b>17</b>	0	65 <sup>e</sup>	35 <sup>f</sup>	A
<b>9</b>	<b>13</b>	<b>17</b>	20-30	20	80	A
<b>9</b>	<b>13</b>	<b>17</b>	60-70	0	100	A
<b>10</b>	<b>13</b>	<b>17</b>	20-30	15 <sup>g</sup>	85 <sup>h</sup>	B
<b>10</b>	<b>13</b>	<b>17</b>	60-70	0	100	B
<b>10</b>	<b>13</b>	<b>18</b>	0	50	40 <sup>i</sup>	B
<b>10</b>	<b>13</b>	<b>18</b>	60-70	0	85 <sup>j</sup>	B
<b>10</b>	<b>14</b>	<b>18</b>	0	40	60	B
<b>10</b>	<b>14</b>	<b>18</b>	60	0	100	B

<sup>a</sup>Obtained by acid cleavage of **19-21**, separated from starting diol, and acetylated for hplc analysis.

<sup>b</sup>The period of lithiation was 0.5-0.75 h.

<sup>c</sup>The period of alkylation was 3-4 h.

<sup>d</sup>Solvent A is water-acetonitrile, 2:3, and solvent B is water-acetonitrile, 3:7.

<sup>e</sup>**9**-Decyn-1-yl acetate has a retention volume ( $V_T$ ) of 9.3 ml.

<sup>f</sup>**9**-Tetradecyn-1-yl acetate has a  $V_T = 29.8$  ml.

<sup>g</sup>**11**-Dodecyn-1-yl acetate has a  $V_T = 9.5$  ml.

<sup>h</sup>**11**-Hexadecyn-1-yl acetate has a  $V_T = 25.6$  ml.

<sup>i</sup>**11**-Tetradecyn-1-yl acetate has a  $V_T = 15.6$  ml and is contaminated with 10% of **11**-hexadecyn-1-yl acetate ( $V_T = 25.6$  ml).

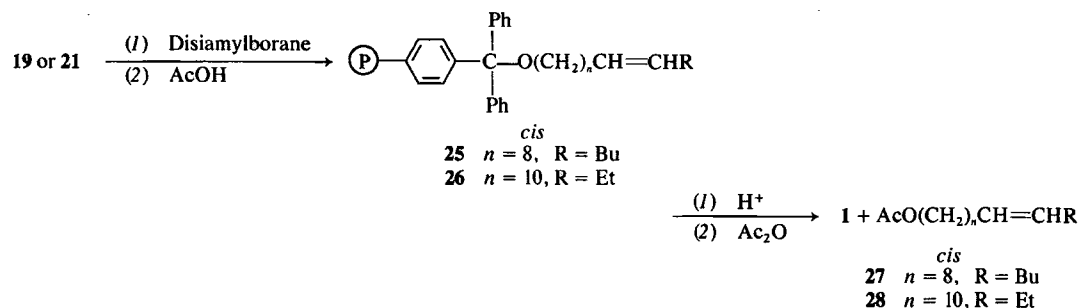
<sup>j</sup>**11**-Tetradecyn-1-yl acetate ( $V_T = 15.6$  ml) is contaminated with 15% of **11**-hexadecyn-1-yl acetate ( $V_T = 25.6$  ml).

identical to their solution analogs in all respects. We make this observation because for this particular reduction a possible explanation is available. In the solution reaction the vinyl borane intermediate, hydrolyzed by protonolysis with acetic acid, yields boron-containing impurities which must be removed by treatment with hydrogen peroxide (**15**). In the analogous reductions of **19** and **21** leading to **25** and **26**, the boron-containing impurities are removed by simple filtration, as the desired products are bound to the insoluble support, and the products **27** and **28** are thus not subjected to treatment with hydrogen peroxide.

#### Elemental Analysis as a Diagnostic Tool for the Determination of Polymer-bound Products

We had previously stated that elemental analyses of polymer-bound products are unreliable

guides to the purity of polymer-bound products (**2**), because, as in all reactions, side products are often obtained along with the desired product and hence polymer-bound products are unlikely to be pure. We prefer to base our yields of reactions on pure products isolated after cleavage from the polymer. Relles and Schluenz partially addressed this problem in discussing polymer-bound phosphine dichlorides (**19**). Firstly, they mention that elemental analysis of polymer-bound phosphorous is unreliable and irreproducible and, secondly, they quantify the amount of reagent bound to the polymer by the job it does and not by the phosphorous content of the polymer, which we feel is reasonable. In our own work in this paper, for example, elemental analysis of one batch of **8** for S (1.65%) shows a sulfur content corresponding to 0.52 mmol of 1,10-decanediol monomesylate/g, but acid cleavage yields only 0.29 mmol of 1,10-decanediol



SCHEME 2

TABLE 3. Yields of sex attractants prepared by reduction of polymer-bound alkynes using various soluble reducing agents

Attractant	Quantity of diol initially bound to polymers 5 and 6 <sup>a</sup> (mmol/g)	Quantity of diol mesylate bound to polymers 7 and 8 <sup>b</sup> (mmol/g)	Quantity of internal alkynols bound to polymers 19 and 21 <sup>c</sup> (mmol/g)	Quantity of diol <sup>e</sup> recovered (mmol/g)	Quantity of alkenol bound to polymers 25 and 26 <sup>d</sup> (mmol/g)	Quantity of alkyne <sup>f</sup> recovered (mmol/g)	Quantity of diol <sup>g</sup> recovered (mmol/g)	Overall yield (%)	Overall conversion <sup>h</sup> (%)
27	0.45	0.22	0.18	0.22	0.18	0	0.20	40 <sup>f</sup>	72
28	0.46	0.22	0.18	0.24	0.17	0	0.23	37	74
28	0.65	0.30	0.25	0.35	0.10 <sup>g,h</sup>	0	0.27 <sup>g,h</sup>	15	42
28	0.65	0.30	0.25	0.35	0.12 <sup>g</sup>	0.07 <sup>g</sup>	0.30 <sup>g</sup>	19	34
28	0.65	0.30	0.25	0.35	0.14 <sup>g,h</sup>	0.06 <sup>g,h</sup>	0.29 <sup>g,h</sup>	21	39

<sup>a</sup>Determined by acid cleavage of 5 and 6.

<sup>b</sup>Determined by acid cleavage of 7 and 8.

<sup>c</sup>Determined by acid cleavage of 19 or 21.

<sup>d</sup>Determined by acid cleavage of 25 or 26.

<sup>e</sup>Yield of diol recovered from acid cleavage of 25 or 26 is recycled.

<sup>f</sup>Solution yield from ref. 10 is 30% based on 8-chloro-1-octanol.

<sup>g</sup>Isolated as their acetates.

<sup>h</sup>The reducing agent caused partial hydrogenolysis in these cases and products were isolated from the filtrate of the reduction of 19 or 21.

monomesylate/g of 8. Indeed recycled polymer 1 contained 0.06 mmol S (0.2%)/g which indicates that a small amount of sulfur-containing product or impurities become permanently bound to the polymer, while a larger fraction of sulfur-containing impurities are washed out during the acid cleavage step or during the procedure used for cleaning recycled 1.<sup>3</sup> Thus elemental analysis of 8 is an unreliable guide to the quantity of 1,10-decanediol monomesylate bound to 8, but does, of course give a maximum possible value. On the other hand elemental analysis for N, of freshly prepared 1 exhibited 0.78 mmol N (1.1%)/g of 1, while recycled 1 still showed 0.29 mmol N (0.41%)/g. Undoubtedly, the nitrogen comes from the *N,N,N',N'*-tetramethylethylenediamine used in the preparation of 1 (12), but the nature and consequences of these irreversibly bound polymer-bound nitrogen-containing impurities is unclear at this time. Recycled 1 also contains 0.42 mmol Cl (1.49%)/g of 1, probably derived from the conversion of 1 to 2 with acetyl chloride, but possibly due to multiple cleavages with HCl in dioxane. Since we can separately analyze for benzylic and trityl chloride by the Volhard method (20) and for aliphatic chloride (2) using potassium *tert*-butoxide, and these methods show no residual chloride for recycled 1, we feel that the residual chloride in recycled 1<sup>4</sup> results from chloride bound to the phenyl rings of 1. Perhaps the surprising aspect of these analytical results lies in the fact that these irreversibly bound impurities do not appear to affect the success of polymer-bound syntheses, although an understanding of these processes will make polymer-bound syntheses even more attractive.

### Conclusions

A total stereoselective synthesis of *cis* insect sex attractants on solid phases has been achieved by a two-step alkyne coupling route using very inexpensive symmetrical diols, acetylene, and alkyl halides. Disiamylborane proved to be the

<sup>3</sup>Bio-Beads SX-2 were used in all reactions. Chemical analysis of the beads as purchased showed 0.91% Cl, 0.68% N, and 0.84% S, while washed beads still showed 0.73% Cl, 0.36% N, and 0.41% S. Thus, non-exhaustive washing procedures do not reduce all of the Cl, N, and S content of the initial polymer, which contribute to unreliable analyses at a later stage.

<sup>4</sup>Polymer 1 has been recycled over 25 times without degradation or significant loss of capacity to bind symmetrical diols.

TABLE 4. High pressure liquid chromatographic analysis<sup>a</sup> of insect attractants,<sup>b</sup> obtained by reduction of polymer-bound alkynes in THF overnight with an excess of various reducing agents at different temperatures

Polymer bound alkyne	Reducing agent	T (°C)	Relative yield of unreduced alkynol <sup>b</sup> (%)	Relative yield of attractant <sup>b</sup> (%)	cis:trans ratio of attractant
19	(Sia) <sub>2</sub> BH	0	0	100 <sup>c</sup>	99:1 <sup>d</sup>
21	(Sia) <sub>2</sub> BH	0	0	100 <sup>e</sup>	90:10 <sup>d</sup>
21	9-BBN <sup>f</sup>	20-30	99.5	0.5	—
21	9-BBN	20-30	17	83	73:27
21	9-BBN	50	0	100	67:33
21	Catechol <sup>g</sup> borane	100 <sup>g</sup>	0	0.5 <sup>h</sup>	—
21	Catechol borane	65	37	63	40:60
21	DIBAH <sup>f</sup>	20-30	94	6	100:0
21	DIBAH	60	26	74	80:20
21	DIBAH <sup>i</sup>	80	0	75 <sup>h,j</sup>	85:15

<sup>a</sup>Solvent B is used (see Table 2, footnote d).

<sup>b</sup>Obtained by cleavage of 25 or 26, separated from starting diol, and acetylated for hplc or vpc analysis.

<sup>c</sup>This entry refers to 27.

<sup>d</sup>These ratios were determined by vpc and hplc analysis. The retention volume (V<sub>T</sub>) of cis-27 is 24.2 ml, trans-27 26.2 ml, cis-28 26.0 ml, and trans-28, 27.4 ml.

<sup>e</sup>This and all lower entries in this column refer to 28.

<sup>f</sup>Only a small excess of reducing agent was used.

<sup>g</sup>This reduction was done in dioxane.

<sup>h</sup>The remaining product was tetradecan-1-yl acetate produced by overreduction.

<sup>i</sup>In benzene.

<sup>j</sup>Complete hydrogenolysis from the polymer occurred and the product was isolated from the filtrate.

only effective reagent capable of converting a polymer-bound alkyne to a *cis* polymer-bound alkene in almost quantitative yield and high stereoselectivity. The polymer-bound products proved to be easier to purify and provided higher yields than reductions performed in solution. Elemental analysis cannot be used to provide quantitative information about polymer-bound products but can provide useful clues to possible side reactions and the presence of polymer-carried impurities.

### Experimental

A Bausch and Lomb Abbé 3L refractometer was used to record the refractive indices. Infrared spectra were recorded on a Unicam SP1000 ir spectrophotometer as neat films between NaCl discs unless otherwise specified. Nuclear magnetic resonance spectra were recorded on a Varian EM360 spectrometer using deuteriochloroform as solvent and tetramethylsilane as internal standard. Mass spectra were recorded on a Perkin-Elmer-Hitachi RMU6E mass spectrometer. Silica gel was used for all thin and preparative layer chromatography. Fractions were extracted with ether in a Soxhlet extractor. Filtration was done under vacuum through sintered glass Buchner funnels. Filtration under an inert atmosphere was done as previously described (2). Microanalyses were performed by G. Gygli of Toronto.

Vapour phase chromatograms were run with a Perkin Elmer 990 instrument using a 15 ft × ¼ in. column of 10% Silar C on Gaschrom Q(60/80) at a temperature of 170°C and a nitrogen flow rate of 15 ml/min. High pressure liquid chromatograms were run with a Waters Asso-

ciates Model 440 instrument, with an R-400 refractive index detector. A 30 × 0.4 cm reverse phase μ Bondapak C-18 column using water-acetonitrile mixtures as solvent was used at a flow rate of 1.0 ml/min. Spectral and analytical data are given for all new compounds and for known compounds where data are unreported.

#### Preparation of Polymer-bound Diol Monomesylates 7 and 8

The polymer-bound monomesylates 7 and 8 were prepared as previously described (2) except that benzene-pyridine, 3:1, was used as solvent instead of pure pyridine in the mesylation steps. This change gives a cleaner, less brown, polymer than previously described.

#### Preparation of Polymer-bound Terminal Alkynes 9 and 10

In a typical experiment, 10.8 ml (25 mmol) of a 2-3 M solution of *n*-butyllithium in 100 ml of dry THF was cooled in a Dry Ice-acetone bath under argon. Dry, acetone free, acetylene was bubbled into the solution for 0.5 h and the solution was stirred for a further 20 min at the Dry Ice bath temperature. To this solution 5 g of 7 or 8, containing 0.25-0.35 mmol of diol monomesylate/g of polymer was added followed by the further addition of 100 ml of HMPT. The mixture was warmed to room temperature and stirred overnight. The black mixture was hydrolyzed with 20 ml of water. The polymer was filtered and washed with three 50 ml portions of ethanol, five 50 ml portions of water, three 25 ml portions of ethanol, and two 50 ml portions of benzene. The polymer, wet with benzene, was transferred to a thimble in a Soxhlet extractor in which molecular sieves (3A) had been placed in a second thimble or in the round bottom flask of the extractor, and the polymer was extracted with benzene for 4 h under reflux conditions. The polymer was washed

free of benzene with dry ether and dried *in vacuo* at 0.2 Torr for 0.5 h. The ir spectra of **9** and **10** exhibited a weak band at  $3400\text{ cm}^{-1}$  ( $\text{C}\equiv\text{C}-\text{H}$ ) and no absorptions at  $1360$  and  $1180\text{ cm}^{-1}$  due to residual mesylate.

#### Preparation of 9-Decyn-1-ol (11) and 11-Dodecyn-1-ol (12) and Their Acetates

A suspension of 1.0 g of **9** in 40 ml of a 0.35 M HCl dioxane solution was stirred at room temperature for 48 h. The polymer residue was washed as previously described (**12**) and the filtrate diluted with water. As the product was somewhat soluble in water it was necessary to isolate the product from the aqueous solution in a liquid-liquid extractor using ether as the organic phase. The ether phase was dried over  $\text{MgSO}_4$  and evaporated to yield 95 mg of crude material. Purification by preparative tlc (eluant, ether-benzene 2:3) afforded, from the slowest moving band ( $R_f$ , 0.15), 47 mg of recovered **3** and, from the faster moving band ( $R_f$ , 0.55), 34 mg of pure 9-decyn-1-ol (**11**), in 38% yield, as an oil;  $n_D^{25}$  1.4851; ir:  $3500$  ( $\text{O}-\text{H}$ ),  $3400$  ( $\text{C}\equiv\text{C}-\text{H}$ ),  $2100$  ( $\text{C}\equiv\text{C}$ ) and  $1050\text{ cm}^{-1}$  ( $\text{C}-\text{O}$ ); nmr  $\delta$ : 3.6 (t, 2,  $J = 7\text{ Hz}$ ,  $\text{CH}_2\text{OH}$ ), 2.2 (m, 2,  $\text{CH}_2\text{C}\equiv\text{C}$ ), 1.9 (t, 1,  $J = 1.5\text{ Hz}$ ,  $\text{C}\equiv\text{C}-\text{H}$ ), and 1.7-1.2 (m, 12,  $(\text{CH}_2)_6$ ). Anal. calcd. for  $\text{C}_{10}\text{H}_{18}\text{O}$ : C 77.87, H 11.76; found: C 76.98, H 11.88.

Acetylation of **11** with acetic anhydride in pyridine yielded 9-decyn-1-yl acetate as an oil; ir:  $3400$  ( $\text{C}\equiv\text{C}-\text{H}$ ),  $2100$  ( $\text{C}\equiv\text{C}$ ),  $1740$  (ester  $\text{C}=\text{O}$ ) and  $1250\text{ cm}^{-1}$  ( $\text{C}-\text{O}$ ); nmr  $\delta$ : 4.0 (t, 2,  $J = 7\text{ Hz}$ ,  $\text{CH}_2\text{O}$ ), 2.2 (m, 2,  $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.0 (s, 3,  $\text{CH}_3\text{CO}$ ), 1.9 (t, 1,  $J = 1.5\text{ Hz}$ ,  $\text{C}\equiv\text{C}-\text{H}$ ), and 1.8-1.2 (m, 12,  $(\text{CH}_2)_6$ ); ms (70 eV)  $m/e$  (relative intensity): 196 (2.6) ( $\text{M}^+$ ), 136 (10) ( $\text{M}^+ - \text{CH}_3\text{CO}_2\text{H}$ ), 43 (100). Anal. calcd. for  $\text{C}_{12}\text{H}_{20}\text{O}_2$ : C 73.43, H 10.27; found: C 73.23, H 10.19.

Similarly (except that liquid-liquid extraction need not be used in this example), **10** yielded 61 mg of recovered **4** and 56 mg of 11-dodecyn-1-ol (**12**), in 43% yield, as an oil (lit. (**21**)  $\text{bp}_{0.005}$   $83-86^\circ\text{C}$ ):  $n_D$  1.4899 (lit. (**21**)  $n_D$  1.4898); ir:  $3500$  ( $\text{O}-\text{H}$ ),  $3400$  ( $\text{C}\equiv\text{C}-\text{H}$ ),  $2100$  ( $\text{C}\equiv\text{C}$ ), and  $1050\text{ cm}^{-1}$  ( $\text{C}-\text{O}$ ); nmr  $\delta$ : 3.6 (t, 2,  $J = 7\text{ Hz}$ ,  $\text{CH}_2\text{O}$ ), 2.2 (m, 2,  $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.0 (s, 3,  $\text{CH}_3\text{CO}$ ), 1.9 (t, 1,  $J = 1.5\text{ Hz}$ ,  $\text{C}\equiv\text{C}-\text{H}$ ), and 1.8-1.2 (m, 16,  $(\text{CH}_2)_8$ ).

Acetylation of **12** as before yielded 11-dodecyn-1-yl acetate as an oil; ir:  $3400$  ( $\text{C}\equiv\text{C}-\text{H}$ ),  $2100$  ( $\text{C}\equiv\text{C}$ ),  $1740$  (ester  $\text{C}=\text{O}$ ), and  $1250\text{ cm}^{-1}$  ( $\text{C}-\text{O}$ ); nmr  $\delta$ : 3.6 (t, 2,  $J = 7\text{ Hz}$ ,  $\text{CH}_2\text{O}$ ), 2.2 (m, 2,  $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.0 (s, 3,  $\text{CH}_3\text{CO}$ ), 1.8 (t, 1,  $J = 1.5\text{ Hz}$ ,  $\text{C}\equiv\text{C}-\text{H}$ ), and 1.8-1.2 (m, 16,  $(\text{CH}_2)_8$ ); ms (70 eV)  $m/e$  (relative intensity): 224 (1) ( $\text{M}^+$ ), 164 (9) ( $\text{M}^+ - \text{CH}_3\text{CO}_2\text{H}$ ), and 43 (100). Anal. calcd. for  $\text{C}_{14}\text{H}_{24}\text{O}_2$ : C 74.95, H 10.78; found: C 74.61, H 10.75.

#### Preparation of Polymer-bound Internal Alkynes 19-21

In a typical experiment, 1.25 g of **10**, containing 0.4 mmol of **12** was suspended in 20 ml of dry THF at  $60-70^\circ\text{C}$  under argon. The mixture was treated with *n*-butyllithium (**13**) (3.5 ml of a 0.5 M solution in hexane, 8 mmol) and stirred at  $60-70^\circ\text{C}$  for 0.5 h. To the suspension was added 5 ml of *n*-butyl bromide (**17**) and 20 ml of HMPT and the mixture was stirred for 4 h at  $60-70^\circ\text{C}$ . The polymer was filtered, washed successively with 10 ml portions of ethanol (three times), water (three times), ethanol (three times), dioxane (three times), and ether (three times), and air dried to give the polymer-bound internal alkyne **20**.

The polymer-bound alkynes did not exhibit absorptions at  $2100-2200\text{ cm}^{-1}$  ( $\text{C}\equiv\text{C}$ ) in their ir spectra.

The formation of **19-21** was achieved to some extent under a variety of conditions and reagents based on the above procedure. These variations are outlined in Table 2.

#### Preparation of Alkyn-1-ols 22-24 and Their Acetates

Acid cleavage of 1.0 g of **20** as previously described (**12**) and filtration and washing of the polymer as before gave a filtrate which was neutralized and evaporated to a mixture of salts and oil. Organic material was extracted with ether dried over  $\text{MgSO}_4$  and evaporated to give an oil. Preparative tlc as before gave 59 mg of recovered **4** and 69 mg of 11-hexadecyn-1-ol (**23**) as an oil;  $n_D$  1.4687; ir:  $3500$  ( $\text{O}-\text{H}$ ) and  $1050\text{ cm}^{-1}$  ( $\text{C}-\text{O}$ ); nmr  $\delta$ : 3.6 (t, 2,  $J = 8\text{ Hz}$ ,  $\text{CH}_2\text{O}$ ), 2.2 (m, 4,  $\text{CH}_2\text{C}\equiv\text{CCH}_2$ ), 1.8-1.2 (m, 20, aliphatic H), and 0.9 (t, 3,  $J = 7.5\text{ Hz}$ ,  $\text{CH}_3\text{CH}_2$ ). Anal. calcd. for  $\text{C}_{16}\text{H}_{30}\text{O}$ : C 80.61, H 12.68; found: C 80.91, H 12.68.

Acetylation of **23** as before yielded 11-hexadecyn-1-yl acetate as an oil;  $n_D$  1.4645; ir:  $1740$  (ester  $\text{C}=\text{O}$ ) and  $1250\text{ cm}^{-1}$  ( $\text{C}-\text{O}$ ); nmr  $\delta$ : 4.0 (t, 2,  $J = 8\text{ Hz}$ ,  $\text{CH}_2\text{O}$ ), 2.2 (m, 4,  $\text{CH}_2\text{C}\equiv\text{CCH}_2$ ), 2.0 (s, 3,  $\text{CH}_3\text{CO}$ ), 1.8-1.2 (m, 20 aliphatic H), 0.9 (t, 3,  $J = 8\text{ Hz}$ ,  $\text{CH}_3\text{CH}_2$ ); ms (70 eV)  $m/e$  (relative intensity): 280 (22) ( $\text{M}^+$ ), 220 (11) ( $\text{M}^+ - \text{CH}_3\text{CO}_2\text{H}$ ), and 43 (100). Anal. calcd. for  $\text{C}_{18}\text{H}_{32}\text{O}_2$ : C 77.09, H 11.50; found: C 77.50, H 11.58.

The yields of **23** and the previously reported (**2**) **22** and **24** are recorded in Table 1. The yields of **22-24** relative to recovered **11** and **12** under different reaction conditions were determined by hplc analysis of their acetates as shown in Table 2.

#### Preparation of Polymer-bound cis-Alkenes 25 and 26

##### Using Diisiamylborane and Other Reducing Agents

A suspension of 1.25 g of **21**, containing 0.3 mmol **24** of **21** was treated with 20 mmol of a 0.5 M THF solution of  $(\text{Si}i\text{a})_2\text{BH}$ . The mixture was stirred at  $-10$  to  $0^\circ\text{C}$  under argon for 4 h, treated with 5 ml of acetic acid, and stirred for a further 0.5 h at  $0-10^\circ\text{C}$ . The polymer-bound *cis*-alkene **26** was filtered, washed with 15 ml portions of water (three times), ethanol (three times), dioxane (three times), and ether (three times), and air dried.

The formation of **25** and **26** was achieved to some extent under a variety of conditions using soluble reducing agents such as 9-BBN, catechol borane, and DIBAH based essentially on the procedure outlined above. The variations on the above conditions are outlined in Table 4.

#### Preparation of cis-9-Tetradecen-1-yl and Acetate (27) and cis-11-Tetradecen-1-ol and Acetate (28)

Insect attractants **27** and **28** were isolated as previously described (**2**) by acid cleavage of **25** and **26** respectively followed by acetylation. The yields of **27** and **28** prepared by different reduction methods are outlined in Table 3. The isomeric purity of **27** and **28** obtained under different reaction conditions was determined by hplc analysis given in Table 4.

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