Synthesis of Insect Sex Attractants on Solid Phases

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Summary Insoluble polymers act as supports in the synthesis of the insect sex attractants, *cis*-dodec-7-enyl acetate, *cis*-tetradec-9-enyl acetate, and *cis*-tetradec-11-enyl acetate.

Insoluble polymer supports have been used in the synthesis of biopolymers such as polypeptides,[1] polynucleotides,[2] and polysaccharides,[3] but have not been employed in the preparation of other types of natural products.

Insect sex attractants[4] of the general formula (**9**) are particularly suitable molecules to prepare on solid phases as symmetrical diols are used as intermediates in their synthesis and we have previously shown that insoluble polymer supports are effective in monoblocking symmetrical diols.[5,6] Thus a 2% cross-linked divinylbenzene–styrene polymer was functionalized to give a polymer-bound trityl chloride (**1**)[7] *via* our direct lithiation method.[6] Polymer (**1**) was treated with the diols (**2a**—**c**) to give the polymer-bound monoprotected diols (**3a**—**c**), respectively. Mesylation of (**3a**—**c**) with $MeSO_2Cl$ in pyridine for 48 h at room temperature gave the polymer bound symmetrical diol monomesylates (**4a**—**c**) respectively, Treatment of (**4a**) and (**4b**) with the lithioacetylene (**5a**), and (**4c**) with (**5b**), in tetrahydrofuran–hexamethylphosphoric triamide (1 : 1) gave the polymer-bound acetylene precursors (**6a**—**c**) to insect sex attractants.[8]

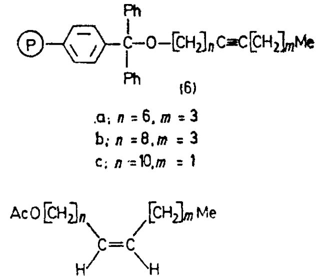
$R^1O[CH_2]_nOR^2$

(2), $R^1 = R^2 = H$
(3), $R^1 = H$, $R^2 = ⓟ$
(4), $R^1 = MeSO_2$, $R^2 = ⓟ$

a; $n = 6$, b, $n = 8$,
c; $n = 10$

$LiC{\equiv}C[CH_2]_mMe$

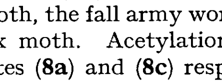
(5)
a; $m = 3$
b; $m = 1$



(6)
a; $n = 6$, $m = 3$
b; $n = 8$, $m = 3$
c; $n = 10$, $m = 1$

$RO[CH_2]_nC{\equiv}C[CH_2]_mMe$

(7); R = H, (8); R = Ac
a; $n = 6$, $m = 3$
b; $n = 8$, $m = 3$
c; $n = 10$, $m = 1$



(9)
a; $n = 6$, $m = 3$
b; $n = 8$, $m = 3$
c; $n = 10$, $m = 1$

Cleavage of (**6a**—**c**) with 0·3 M HCl in dioxan gave the acetylenic alcohols (**7a**—**c**), respectively and polymer-bound trityl alcohol (**10**). In all cases some unchanged symmetrical diol and symmetrical diol monomesylates were recovered. Hydrogenation of (**7b**) gave the *cis*-alcohol $HO[CH_2]_8CH{=}CH[CH_2]_3Me$, which on acetylation afforded in high yield (Table) the *cis*-acetate (**9b**),[9] the sex attractant of the southern army worm moth, the fall army worm moth, and the summer fruit tortrix moth. Acetylation of (**7a**) and (**7c**) gave the ynyl acetates (**8a**) and (**8c**) respectively.

Table

Insect Attractant	Insect	Quantity of diol initially bound to polymers (**3a**—**c**)[a] (mmol g^{-1})	Quantity of attractant produced (mmol g^{-1})	Overall yield (%)	Overall conversion[b]
(**9a**)	Cabbage looper	0·44	0·12	27	57
(**9b**)	Southern army worm, fall army worm, summer fruit tortrix moth	0·42	0·15	36	52
(**9c**)	Red banded leaf roller	0·52	0·19	36	53

[a] Determined by cleavage with 0·3 M HCl in dioxan of samples of (**3a**—**c**). [b] Yield, if recovered diol and mesylate are recycled.

Hydrogenation[8] of (**8a**) and (**8c**) gave in high yields (Table) the *cis*-acetate[10] (**9a**), the sex attractant of the cabbage looper, and the *cis*-acetate[11] (**9c**), the sex attractant of the red banded leaf roller, respectively. All spectroscopic and analytical data of (**9a**—**c**) confirmed the structures of these known compounds. The mass spectra, taken at an ionization potential of 16 eV, of (**9a**—**c**) exhibited weak, but detectable parent ions and base peaks corresponding to loss of acetic acid. The polymer (**10**) recovered from the synthetic scheme can readily be converted into (**1**) and recycled.

The polymer-support method of synthesis gives comparable or better overall yields than previous methods, uses inexpensive symmetrical diols as starting materials, and has the potential for being adapted to an automated procedure.[1]

We thank the National Research Council of Canada for support.

(*Received*, 12*th January* 1976; *Com.* 020.)

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