

JOURNAL OF THE CHEMICAL SOCIETY

PERKIN TRANSACTIONS I Organic and Bio-organic Chemistry

Reaction of Dialdehydes with Conventional and Polymer-supported Wittig Reagents

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Olefinizations carried out under a variety of conditions, using a 1 : 1 molar ratio of polymer-supported Wittig reagent to dialdehyde (terephthalaldehyde and isophthalaldehyde), lead exclusively to monocondensation products. Results in conventional reactions, depend on the particular Wittig reagent employed, the procedure used, and the halide counterion which is present: when using ethylene oxide as base, chloride ion favours mono-olefinizations. In solid phase Wittig reactions, with ethylene oxide as base and bromide as the counterion, monoethylene acetal formation becomes an important by-reaction.

ONCE the fruitful application of insoluble polymer-supported Wittig reagents had been established,¹ there

The Table summarizes our work on the above subject and gives the results of conventional condensations

Results of conventional and solid-phase Wittig reactions

Reaction no.	Technique ^a	Procedure ^b	Reagent ^c	Aldehyde ^d	Reactants ratio ^e	Products ratio ^f	Total yield (%) ^g
I	M	A	MB	T	1	12.6	84
II	M	A	MB	T	2	0.43	82
III	M	C	MB	T	1	∞	99 ^h
IV	M	C	MB	T	2	0	79
V	M	C	MC	T	2	0.41	67
VI	P	C	MB	T	1	∞	93 ^h
VII	P	D	MB	T	1	∞	98 ^h
VIII	P	D	MC	T	1	—	—
IX	P	D	MB	I	1	∞	27 ^h
X	M	B	BC	T	1	0	83
XI	M	B	BC	T	2	0	80
XII	P	B	BC	T	1	∞	24
XIII	P	B	BB	T	1	∞	83
XIV	P	B	BB	T	2	3.45	60
XV	P	C	BB	T	1	∞	85 ⁱ
XVI	P	C	BC	T	1	∞	63 ^h
XVII	P	C	BC	T	2	3.1	57
XVIII	P	C	BB	I	1	∞	67
XIX	M	C	BB	T	2	∞	23
XX	M	C	BB	T	2	0.04	94
XXI	M	C	BC	T	2	∞	100
XXII	M	C	BC ^j	T	2	0	99
XXIII	M	C	BC	I	2	0	99

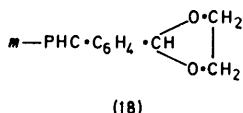
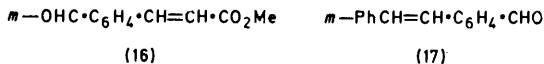
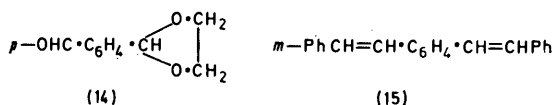
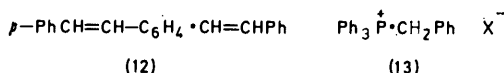
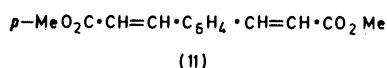
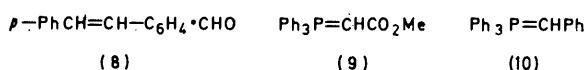
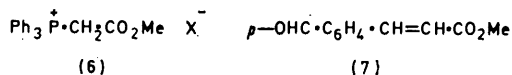
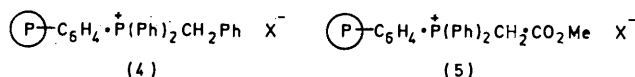
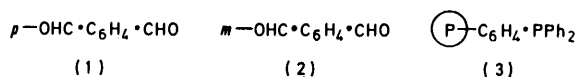
^a M, conventional (monomeric) and P, solid phase (polymeric). ^b See text. ^c MB, methyl bromoacetate, MC, methyl chloroacetate; BB, benzyl bromide; BC, benzyl chloroacetate. ^d T, terephthalaldehyde. I, Isophthalaldehyde. ^e Molar ratio of Wittig reagent, or Wittig functionality, to dialdehyde. ^f Molar ratio of mono-olefinization products to diolefinization products. ^g Yield based on aldehyde or on Wittig reagent, or functionality, depending on which of the two was present in a lesser proportion. ^h Yield based on unrecovered aldehyde. ⁱ Yield based on unacetalized aldehyde. ^j Tetrabutylammonium bromide was added.

appeared to us that the 'functional group fixation' and 'high dilution behaviour' to be expected of polymeric reagents,² could be exploited to effect mono-olefinizations of dialdehydes, such as terephthalaldehyde (1) and isophthalaldehyde (2).

which were performed in order to provide comparative data.

Polymer-supported Phosphonium Salts.—The starting material for the preparation of insoluble polymer-supported Wittig reagents is cross-linked diphenyl-

polystyrylphosphine (3) which, here, has been prepared by (i) reaction of cross-linked bromopolystyrene³ with



lithium diphenylphosphide and (ii) reaction of cross-linked polystyryl-lithium with chlorodiphenylphosphine.^{1b,3} In our opinion, now that cross-linked polystyryl-lithium can be prepared directly by reaction of cross-linked polystyrene with the 1:1 complex of *n*-butyl-lithium and *NNN'*-tetramethylethylenediamine,⁴ method (ii) should be the more convenient one. (Since only cross-linked polymers have been used throughout this work, hereafter the qualifying adjective will be dropped).

Benzylidiphenylpolystyrylphosphonium chloride (4; X = Cl)^{1a} and bromide (4; X = Br) are prepared without difficulty by heating (3) with benzyl chloride and benzyl bromide, respectively. However, preparation of methoxycarbonylmethylidiphenylpolystyrylphosphonium bromide (5; X = Br) by refluxing (3) with a benzene solution of methyl bromoacetate was unsuccessful. This failure was understood when the thermal instability of (1-methoxycarbonylalkyl)triphenylphosphonium bromides⁵ was fully realized and further investigated in our own laboratories.⁶

In agreement with these observations, polymer phosphonium salt (5; X = Br) was finally prepared, in a satisfactory way, by shaking at room temperature for 168 h, a suspension of (3) in a mixture of benzene and methyl bromoacetate. At this point, it is worth remembering that quaternizations of triphenylphosphine with methyl bromoacetate and methyl chloroacetate to give the corresponding methoxycarbonylmethyltriphenylphosphonium halides (6; X = Br or Cl)⁷ are also effected at room temperature.

Wittig Reaction Procedures.—In both, the conventional or monomeric (designated by M in the Table) and the solid phase or polymeric (designated by P) techniques, several procedures are available for carrying out a desired Wittig reaction. In the sequel, capital letters are those used in the Table.

A. The Wittig reagent is prepared in a previous operation and stored. This is only possible with stable Wittig reagents.

B. The Wittig reagent is prepared *in situ* from the phosphonium salt and a strong base. The need of good solvents, which solubilize the base and swell the polymer, puts limits to using this procedure in solid phase technique. We find butyl-lithium to be the base more generally employable.

C. The Wittig reagent is progressively generated *in situ*, in the presence of the aldehyde, from phosphonium salt and ethylene oxide as base, following Buddrus findings.⁸ This procedure is quite convenient in solid phase work.

D. The phosphonium salt, that will give rise to the Wittig reagent, is progressively generated *in situ* from phosphine and alkyl halide, in the presence of ethylene oxide and the aldehyde.⁸ We have found this to be the procedure of choice for solid-phase Wittig reactions.

Mono- versus Di-olefinization.—The problem of mono- versus di-olefinization of dialdehydes has been approached by Leznoff *et al.*⁹ by using polymer-bound 1,3-diols as monoprotecting groups.

Our own results on both solid phase and conventional work on mono- *vs.* di-olefinization of dialdehydes, are collected in the Table and can be summarized as follows.

(i) *Solid-phase technique (reactions marked P in the Table).* An important general conclusion emerges from reactions VI—IX, XII, XIII, XV, XVI, and XVIII, in which polymeric Wittig reagents, obtained by different procedures, were present in a 1:1 molar ratio *vs.* the dialdehyde. Under these conditions, only mono-olefinization reactions took place. This exclusive mono-olefinization has to be attributed to the blocking of all the active sites by formation of a betaine intermediate with one of the two carbonyl groups of the dialdehyde.

It is significant, too, that in reactions XIV and XVII, in spite of using benzylphosphorane and dialdehyde in a 2:1 molar ratio, mono-olefinization took place in more than 75%.

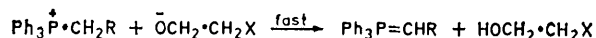
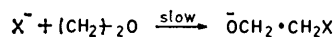
(ii) *Conventional technique (reactions marked M in the Table).* (Reactions carried out using Buddrus procedures are commented upon in next section). The

high proportion of monoreaction products observed in reactions I and III, and the absence of them in reaction X, in spite of using in all cases a 1:1 molar ratio of phosphorane to dialdehyde, can be explained by the following reasons. (a) Because of the influence of the other carbonyl group, a carbonyl group in terephthalaldehyde should be more reactive than one on the mono-olefinization products methyl *p*-formylcinnamates (7) and *p*-styrylbenzaldehydes (8).¹⁰ (b) The lesser reactivity of methoxycarbonylmethylidetriphenylphosphorane (9) as compared with benzylidetriphenylphosphorane (10), makes the former much more 'carbonyl-discriminating' than the latter.

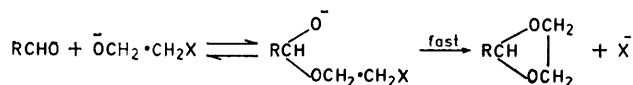
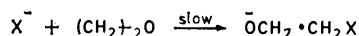
When a 2:1 molar ratio is used, the phosphorane (9) still discriminates between two carbonyl groups of different nature and, thus, in reaction II, together with the diester (11), some mono-olefinization product is isolated while, in reaction XI, the phosphorane (10) leads exclusively to the diolefinization products *p*-styrylstilbenes (12).

Several related examples of the use of phosphorane (9) in mono-olefinization reactions can be found in the literature¹¹ and a monoreaction of phthalaldehyde with benzylidetriphenylphosphorane (10), using a 5:1 molar ratio, has also been reported.¹²

Wittig-Buddrus Reactions.—According to Buddrus,⁸ phosphonium salts such as methoxycarbonylmethyltriphenylphosphonium halides (6) and benzyltriphenylphosphonium halides (13), here jointly represented by $\text{Ph}_3\text{P}^+\text{CH}_2\text{R X}^-$, are converted by ethylene oxide into the corresponding phosphoranones, $\text{Ph}_3\text{P}=\text{CHR}$, through intermediate formation of halogenoethoxide anions (Scheme 1). If present in sufficient quantity, the halogeno-



SCHEME 1



SCHEME 2

ethoxide anion can act also as catalyst of the formation of ethylene acetals from aldehyde and ethylene oxide,^{8b,13} a reaction which can compete with the Wittig condensation. An acceptable mechanism for acetal formation is given in Scheme 2.

The substantial formation of the ethylene acetal (14) which took place in reaction XV, can be explained by the action of several favourable factors: (a) the use of a preformed phosphonium salt (type C procedure) which implies a high halide concentration; (b) the use of bromide as counterion which, as a consequence of bromide being a better nucleophile than chloride, warrants a

relatively high concentration of $\text{XCN}_2\text{-CH}_2\text{O}^-$; (c) the lower acidity of benzylphosphonium halides, as compared with methoxycarbonylmethylphosphonium halides, which allows a higher concentration of halogenoethoxide anions; and (d) the use of a polymer supported phosphonium salt which is thought to be less accessible than the corresponding monomeric salt and, consequently, to react more slowly with the halogenoethoxide anion.

Conventional reactions IV and V, and XIX—XXII, in all of which phosphorane and dialdehyde were used in a molar ratio 2:1, reflect important differences in the ratio of mono- to di-olefinization products, depending on the nature of the halide counterion; these differences must be due to the lower concentration of $\text{XCH}_2\text{-CH}_2\text{O}^-$ when $\text{X} = \text{Cl}$. Special mention deserves the exclusive formation of monocondensation products (8) in reaction XXI, in which benzyltriphenylphosphonium chloride (13; $\text{X} = \text{Cl}$) was used, and the fact that addition of tetrabutylammonium bromide (reaction XXII) led to the exclusive formation of dicondensation products (12).

Probably, the failure of reaction VIII was due to lack of reaction between diphenylpolystyrylphosphine and methyl chloroacetate, under the conditions employed.

EXPERIMENTAL

All melting points were determined on a Kofler microscope and are uncorrected. I.r. spectra (not reported) were recorded on a Perkin-Elmer Infracord 720 or on a Pye Unicam SP 1100 i.r. spectrophotometer using KBr discs. N.m.r. spectra were measured on a Perkin-Elmer R-12 (60 MHz) spectrometer using tetramethylsilane as an internal standard and deuteriochloroform as solvent, unless otherwise stated; chemical shifts are given in the τ scale. Mass spectra were registered in a Hewlett-Packard mass spectrometer, model 5930 A, working at 70 eV and coupled to a Hewlett-Packard gas chromatograph model 5700 A. Gas-chromatographic analyses were performed on a Perkin-Elmer F-12 instrument with a flame ionization detector. Solvents were removed on a Büchi Rotavapor-R. Small amounts of high-boiling substances were distilled on a Büchi glass tube oven. Polymer lithiations were carried out in a special reactor with a sinter-glass bottom, in which liquids were maintained by means of a 'compensating gas pressure' system; by reducing the gas pressure, filtration ensued. Nitrogen or argon atmospheres and carefully redistilled and conveniently dried solvents were used throughout.

No elemental analyses are given for the new compounds Z-(7), Z-(8), (14), *E,E*-(15), *E,Z*-(15), *Z,Z*-(15), *E*-(16), and Z-(17); their way of formation and spectral data being taken as sufficient for their characterization.

Preparation of Bromopolystyrene.³—Bromine (20.5 g, 128 mmol) was added dropwise to a well stirred suspension of 2% cross-linked polystyrene beads (40.00 g, 200—400 mesh, from Dow, Chemical Co.) and thallium(III) acetate¹⁴ (15.00 g, 39 mmol; prepared from dithallium trioxide and aqueous acetic acid) in carbon tetrachloride (500 ml). After complete decoloration, the polymer was filtered off and washed with dioxan, aqueous 1M-HCl, water until pH 7, and then three times with methanol, dioxan, and ether.

Finally, the polymer, bromopolystyrene, was dried over potassium hydroxide and phosphorus pentoxide, at 1 Torr and 80 °C, until constant weight (45.03 g). Elemental analysis: 19.8% of bromine, equivalent to 2.47 mequiv. Br/g polymer. In other runs, 2.18, 2.15 and 2.27 mequiv. Br/g polymer were found. I.r. (ν_{\max}): 3 025, 2 920, 1 580, 1 460, 1 430, 1 060, 1 010, 820, 750, and 700 cm^{-1} .

Preparation of Diphenylpolystyrylphosphine (3).—Method 1. An ether solution (210 ml) of butyl-lithium (211 mmol) was added dropwise, at -10 °C, with vigorous stirring, to a suspension of bromopolystyrene (20.00 g; 2.15 mequiv. Br/g polymer; 43 mmol of functionality) in toluene (400 ml). The mixture was stirred for 24 h at -10 °C and then, at the same temperature, the polymer was filtered off, washed with toluene, and suspended again in toluene. To the well stirred suspension, kept at -10 °C, chlorodiphenylphosphine (28.00 g, 126 mmol) was added slowly and the mixture was left for 15 h at -10 °C. The polymer was filtered off and washed several times with dioxan, water, dioxan, and ether. Finally, the polymer, *diphenylpolystyrylphosphine (3)*, was dried as in the preparation of bromopolystyrene (17.89 g). Elemental analysis: 2.3% of residual bromine and 4.20% of phosphorus, equivalent to 1.35 mequiv. P/g polymer. I.r. (ν_{\max}): 3 050, 2 950, 1 670, 1 600, 1 490, 1 450, 1 190, 1 125, 1 030, 750, and 690 cm^{-1} .

Method 2. Chlorodiphenylphosphine (65.42 g, 297 mmol) was added dropwise to a suspension of finely divided lithium (18.10 g, 2.59 mol) in tetrahydrofuran (500 ml).¹⁵ The deep red solution was stirred for 3 h at room temperature and then refluxed for 1 h; bromopolystyrene (40.00 g; 2.47 mequiv. Br/g polymer; 98.8 mmol of functionality) was then added to it. The reaction mixture was then kept at room temperature for 2 days, with vigorous stirring. The observable excess of lithium was removed and the polymer was filtered off and washed four times with tetrahydrofuran, water, methanol, benzene, and ether. Finally, the polymer, *diphenylpolystyrylphosphine (3)*, was dried as in the preparation of bromopolystyrene (32.57 g). Elemental analysis: 5.61% of phosphorus, equivalent to 1.80 mequiv. P/g polymer.

Preparation of Methoxycarbonylmethyldiphenylpolystyrylphosphonium Bromide (5; X = Br).—A suspension of the polymer (3) (5.00 g, 1.79 mequiv. P/g polymer; 8.95 mmol of functionality) in a mixture of methyl bromoacetate (5.00 g, 32.6 mmol) and benzene (15 ml) was shaken for 7 days at room temperature. The polymer was filtered off and washed several times with benzene and ether. Finally, the polymer, *methoxycarbonylmethyldiphenylpolystyrylphosphonium bromide (5; X = Br)* was dried as in the preparation of bromopolystyrene (6.33 g). Elemental analysis: 4.04% of phosphorus and 10.68% of bromine, equivalent to 1.33 mequiv. Br/g polymer. I.r. (ν_{\max}): 3 300, 3 030, 2 925, 1 720, 1 590, 1 490, 1 440, 1 110, 1 020, 950, and 690 cm^{-1} .

Preparation of Benzyldiphenylpolystyrylphosphonium Bromide (4; X = Br).—A suspension of polymer (3) (5.00 g; 1.79 mequiv. P/g polymer; 8.95 mmol of functionality) in a mixture of benzyl bromide (10.00 g, 58 mmol) and benzene (25 ml) was refluxed for 16 h and then left at room temperature overnight. The polymer was filtered off and washed several times with benzene and ether. Finally, the polymer, *benzyldiphenylpolystyrylphosphonium bromide (4; X = Br)*, was dried as in the preparation of bromopolystyrene (6.48 g). Elemental analysis: 3.68% of phosphorus and 10.03% of bromine, equivalent to 1.25 mequiv. Br/g poly-

mer. I.r. (ν_{\max}): 3 300, 3 050, 2 925, 1 600, 1 490, 1 440, 1 190, 1 105, 1 020, 950, and 690 cm^{-1} .

Preparation of Benzyldiphenylpolystyrylphosphonium Chloride (4; X = Cl).—A suspension of polymer (3) (7.35 g; 1.27 mequiv. P/g polymer; 9.33 mmol of functionality) in benzyl chloride (19.24 g, 152 mmol) was refluxed for 5 h. The polymer was filtered off and washed several times with benzene and ether. Finally, the polymer, *benzyldiphenylpolystyrylphosphonium chloride (4; X = Cl)*, was dried as in the preparation of bromopolystyrene (8.00 g). Elemental analysis: 3.58% of phosphorus and 2.26% of chlorine, equivalent to 0.64 mequiv. Cl/g polymer.

Monomeric Procedure A Reactions.—Reaction I. A solution of (1) (782 mg, 5.85 mmol) in dimethoxyethane (20 ml) was added slowly, with vigorous stirring, to the ylide (9)⁷ (2.000 g, 5.90 mmol) dissolved in dimethoxyethane (60 ml). After refluxing for 5 h, the mixture was left at room temperature for 16 h. Removal of solvent gave a residue which was chromatographed on silica gel, using methylene chloride-diethyl ether (98 : 2) as eluant. In this way, methyl (*E*)-*p*-formylcinnamate, *E*-(7) (861 mg, 4.53 mmol), m.p. 79–82 °C [lit. (unspecified stereochemistry),¹⁶ 79–81 °C]; n.m.r. -0.03 (s, 1 H), 2.04, 2.18, 2.31, and 2.44 (AA'BB', 4 H), 2.31 (part A of an AB system, $J = 16$ Hz, 1 H), 3.51 (part B of an AB system, $J = 16$ Hz, 1 H), 6.20 (s, 3 H and (*E,E*)-1,4-bis(2-methoxycarbonylvinyl)benzene, *E,E*-(11) (88 mg; 0.36 mmol), m.p. 184–186 °C [lit. (unspecified stereochemistry)¹⁷ 166–170°], n.m.r.; 2.36 (part A of an AB system, $J = 16$ Hz, 2 H), 2.52 (s, 4 H), 3.57 (part B of an AB system, $J = 16$ Hz, 2 H), 6.23 (s, 6 H), were obtained; total yield 84%.

Reaction II. Reactants: 422 mg (3.20 mmol) of (1) and 2.165 g (6.40 mmol) of (9). Products: 150 mg (0.79 mmol) of *E*-(7) and 453 mg (1.84 mmol) of *E,E*-(11); total yield 82%.

Monomeric Procedure B Reactions.—Reaction X. Sodium methoxide [prepared by treating sodium (327 mg; 14.2 g-atom) with dry methanol (50 ml) and removing the excess of methanol under reduced pressure] was dissolved in dimethoxyethane (50 ml) and then the phosphonium salt (13; X = Cl) (5.517 g, 14.2 mmol) was added with vigorous stirring; the solution turned orange. Compound (1) (1.903 g, 14.2 mmol) was added and a progressive discoloration was observed. The reaction mixture was stirred for 3 h and left aside for a further 15 h. Direct filtration afforded (*E,E*)-*p*-styrylstilbene, *E,E*-(12), m.p. 263–264 °C (lit.,¹⁸ 266–267 °C) (n.m.r. spectrum not registered because of the insolubility of the compound in the available solvents), and a solution from which solvents were removed under reduced pressure. The resulting solid mixture was fractionally crystallized from methanol and in this way (*Z,E*)-*p*-styrylstilbene, *Z,E*-(12), m.p. 121–123 °C (lit.,¹⁸ 114–114.5 °C), n.m.r.: 2.6–2.82 (complex absorption, 14 H), 3.06 (s, 2 H), and 3.51 (s, 2 H), further *E,E*-(12), and a residual mixture were obtained. This mixture was resolved by chromatography on silica gel, using carbon tetrachloride as eluant, into (*Z,Z*)-*p*-styrylstilbene, *Z,Z*-(12), oil (lit.,¹⁸ m.p. 85.5–87.5 °C); n.m.r.: 2.89 (s, 10 H), 2.99 (s, 4 H), and 3.53 (s, 4 H), *Z,E*-(12) and *E,E*-(12).

The combined amounts of isolated substances were as follows: *E,E*-(12) 228 mg (0.8 mmol), *Z,E*-(12) 650 mg (2.3 mmol), and *Z,Z*-(12) 781 mg (2.8 mmol). Total yield, based on theoretical mols of diolefinization products, 83%.

Reaction XI. Reactants: 335 mg (14.5 g-atom) of sodium, 5.633 g (14.0 mmol) of phosphonium salt (13);

X = Cl) and 971 mg (7.2 mmol) of (1). Products: *E,E*-(12): 534 mg (1.89 mmol); *Z,E*-(12): 586 mg (2.08 mmol); *Z,Z*-(12): 512 mg (1.81 mmol); total yield 80%.

Monomeric Procedure C Reactions.—**Reaction III.** The phosphonium salt (6; X = Br)⁷ (1.825 g, 4.4 mmol) and (1) (587 mg, 4.4 mmol) were dissolved in methylene chloride (40 ml) contained in a small pressure-resistant glass reactor. The mixture was cooled to 0 °C, and ethylene oxide (2.00 g; 44 mmol) was added to it; the vessel was then closed and heated at 45–50 °C for 45 h. Removal of solvents gave a residue which was chromatographed on silica gel, using methylene chloride–carbon tetrachloride (3 : 1) and methylene chloride as eluants: most of the fractions consisted of *E*-(7), which was recrystallized from hexane. Fractions consisting of mixtures were qualitatively and quantitatively (peak area measurements) analysed by g.l.c., showing that (1), methyl (*Z*)-*p*-formylcinnamate, *Z*-(7), n.m.r. [as deduced from a spectrum of a mixture with *E*-(7)] 0.04 (s, 1 H), 2.09, 2.23, 2.35, 2.49 (AA'BB' system, 4 H), 3.05 (part A of an AB system, *J* = 12 Hz, 1 H), 4.14 (part B of an AB system, *J* = 12 Hz, 1 H), and 6.43 (s, 3 H), *E*-(7), and *E,E*-(11) had been eluted in that order. Product composition of the reaction mixture was estimated to be as follows: (1) (72 mg, 0.54 mmol), *Z*-(7), (12 mg, 0.06 mmol), *E*-(7) (715 mg, 3.76 mmol), and *E,E*-(11) (traces); total yield 87%. Total yield based on unrecovered (1): 99%. G.l.c. conditions: 2 m × 0.5 in column; DEGS on Chromosorb X-AW-DMCS-60/80; programmed temperature from 150 to 170 °C; nitrogen pressure of 1.2 kg/cm².

Reaction IV. Reactants: 492 mg (3.7 mmol) of (1), 3.052 g (7.35 mmol) of (6; X = Br), and 2.00 g (44 mmol) of ethylene oxide. The crude reaction mixture was recrystallized from carbon tetrachloride (20 ml) to give 721 mg (2.9 mmol) of *E,E*-(11); yield 79%.

Reaction V. Reactants: 379 mg (2.8 mmol) of (1), 2.098 g (5.6 mmol) of (6; X = Cl) and 2.00 g (44 mmol) of ethylene oxide. The crude reaction mixture was recrystallized from carbon tetrachloride to give 233 mg (0.95 mmol) of *E,E*-(11). Combined chromatographic separation (silica gel–methylene chloride) and fractional crystallization (hexane) led to a further 93 mg (0.38 mmol) of *E,E*(11) and 104 mg (0.55 mmol) of *E*-(7); total yield 67%.

Reaction XXI. Reactants: 2.960 g (7.62 mmol) of phosphonium salt (13; X = Cl), 525 mg (3.91 mmol) of (1), and 3.00 g (66 mmol) of ethylene oxide. Products: 222 mg (1.07 mmol) of pure (*E*)-*p*-styrylbenzaldehyde, *E*-(8), m.p. 110–112 °C [lit. (unspecified stereochemistry)¹⁹ 101–105 °C], n.m.r. (CCl₄): 0.20 (s, 1 H), 2.72, 2.38, 2.49, 2.62 (AA'BB' system, 4 H), 2.55–3.00 (complex absorption, 7 H); 312 mg (1.50 mmol) of a 9 : 1 mixture (g.l.c. analysis) of (*Z*)-*p*-styrylbenzaldehyde, *Z*-(8), n.m.r. [as deduced from a spectrum of a mixture with *E*-(8)]: 0.15 (s, 1 H), 2.32, 2.46, 2.67, 2.81 (AA'BB' system, 4 H), 2.90 (s, 5 H), 3.32, 3.52 (AB system, *J* = 12 Hz, 2 H), and *E*-(8); and 278 mg (1.34 mmol) of a 1 : 1 mixture (g.l.c. analysis) of *Z*-(8) and *E*-(8); total yield 100%.

Reaction XIX. Reactants: 2.300 g (4.9 mmol) of (13; X = Br), 329 mg (2.46 mmol) of (1), and 2.00 g (44 mmol) of ethylene oxide. Exceptionally, the reaction time was 6 h. Products: 116 mg (0.55 mmol) of a mixture of the *p*-styrylbenzaldehydes (8); 250 mg (1.86 mmol) of (1); yield 23% [yield based on unrecovered (1) 100%].

Reaction XX. Reactants: 3.132 g (7.2 mmol) of (13; X = Br), 484 mg (3.6 mmol) of (1), and 3.00 g (66 mmol)

of ethylene oxide. Products: 29 mg (0.14 mmol) of a mixture of the *p*-styrylbenzaldehydes (8); 95 mg (0.34 mmol) of *E,E*-(12); 208 mg (0.74 mmol) of *Z,E*-(12); 618 mg (2.19 mmol) of a mixture consisting of *Z,E*-(12) and *Z,Z*-(12); total yield 94%.

Reaction XXII. Reactants: 2.500 g (6.43 mmol) of (13; X = Cl), 431 mg (3.21 mmol) of (1), 3.00 g (66 mmol) of ethylene oxide, and 2.07 g (6.43 mmol) of tetrabutylammonium bromide. Products: 899 mg (3.19 mmol) of a mixture of the *p*-styrylstilbenes (12); total yield 99%.

Reaction XXIII. Reactants: 3.000 g (7.72 mmol) of the phosphonium salt (13; X = Cl), 517 mg (3.86 mmol) of (2) and 3.00 g (66 mmol) of ethylene oxide. After 24 h, an aliquot was withdrawn and solvents were removed under reduced pressure. Addition of carbon tetrachloride gave a solid, identified as unchanged (13; X = Cl), and a solution which was chromatographed on silica gel, using carbon tetrachloride and carbon tetrachloride–methylene chloride (1 : 1) as eluants. Products: 82 mg (0.29 mmol) of a mixture of *m*-styrylstilbenes, (15), and 79 mg (0.38 mmol) of a mixture of *m*-styrylbenzaldehydes, (17). This mixture was chromatographed to afford pure (*Z*)-*m*-styrylbenzaldehyde, *Z*-(17), as an oil, n.m.r.: 0.23 (s, 1 H), 2.28–2.90 (complex absorption, 4 H), 2.92 (s, 5 H), and 3.43 (s, 2 H), and pure (*E*)-*m*-styrylbenzaldehyde, *E*-(17), m.p. 101–103 °C [lit. (unspecified stereochemistry)¹⁹ 104–107 °C], n.m.r. (CCl₄): 0.04 (s, 1 H), and 1.91–2.87 (complex absorption, 11 H).

The remaining reaction mixture was kept at 45–50 °C for a further 48 h. After removal of solvents under reduced pressure, addition of carbon tetrachloride gave a solid, which was identified as triphenylphosphine oxide, and a solution which was chromatographed on silica gel, using carbon tetrachloride as eluant. In this way, a mixture (883 mg, 3.13 mmol) was obtained that consisted of (*E,E*)-*m*-styrylstilbene, *E,E*-(15) (0.41 mmol), m.p. 166–170 °C, n.m.r.: 2.33–2.84 (complex absorption, 15 H), 2.92 (s, 3 H), (*Z,E*)-*m*-styrylstilbene, *Z,E*-(15) (1.41 mmol), m.p. 55–57 °C, n.m.r.: 2.30–2.95 (complex absorption, 14 H), 3.09 (s, 2 H), 3.42 (s, 2 H), and (*Z,Z*)-*m*-styrylstilbene, *Z,Z*-(15) (1.31 mmol), oil, n.m.r. (CCl₄): 2.88 (s, 11 H), 3.00 (s, 3 H), and 3.53 (s, 4 H); total yield (including products from the aliquot previously withdrawn) 99%.

Polymeric Procedure B Reactions.—**Reaction XIII.** A 1.1M-ether solution (6.0 ml) of butyl-lithium was added dropwise to a well stirred suspension of the polymer (4; X = Br) (816 mg, 0.93 mequiv. Br/g polymer; 0.76 mmol of functionality) in tetrahydrofuran (40 ml). After 90 min, (1) (123 mg; 0.92 mmol) was added and the mixture was stirred overnight at room temperature and then refluxed for 6 h. The polymer was filtered off and carefully washed with methylene chloride and ether; these washings were combined with the main solution. After removal of solvents, the residue was taken up in methylene chloride (50 ml) and the solution was washed with water (3 × 50 ml). The organic layer was dried and distilled and the residue solid was crystallised from carbon tetrachloride to give a mixture (130 mg) of *Z*-(8) (104 mg, 0.5 mmol) and *E*-(8) (26 mg, 0.13 mmol); total yield 83%.

Reaction XII. Reactants: 3.393 g (0.65 mequiv. Cl/g polymer; 2.16 mmol of functionality) of polymer (4), 58 mg (2.43 mmol) of sodium hydride in tetrahydrofuran (20 ml), 326 mg (2.43 mmol) of (1) in tetrahydrofuran (10 ml). Products: mixture (108 mg) of *Z*-(8) (43 mg, 0.21 mmol) and *E*-(8) (65 mg, 0.31 mmol); total yield 24%.

p-Hydroxymethylbenzaldehyde (42 mg) was also identified.¹⁹

Reaction XIV. Reactants: 1.618 g (0.93 mequiv. Br/g polymer; 1.51 mmol of functionality) of polymer (4; X = Br), 10 ml of a 1.1M-ether solution of butyl-lithium (after 2 h, excess reagent was filtered off, the polymer-ylide was washed with tetrahydrofuran and, finally, it was suspended in tetrahydrofuran), 122 mg (0.91 mmol) of (1). Products: mixture (118 mg) consisting of *p*-styrylbenzaldehydes (8) (79 mg, 0.38 mmol), *p*-styrylstilbenes, (12) (31 mg, 0.11 mmol), and *p*-hydroxymethylbenzaldehyde¹⁹ (8 mg, 0.06 mmol); total yield 60%.

Polymeric Procedure C Reactions.—Reaction VI. Polymer (5; X = Br) (2.550 g; 1.33 mequiv. Br/g polymer; 3.32 mmol of functionality) was suspended in a mixture of (1) (509 mg, 3.80 mmol) and benzene (60 ml) contained in a small pressure-resistant glass reactor. After the mixture had been cooled to 0 °C, ethylene oxide (1.70 g, 40.0 mmol) was added and the vessel was closed and shaken at room temperature for 68 h and then heated at 45–50 °C for 6 h. The polymer was filtered off and carefully washed with methylene chloride and ether; these washings were combined with the main benzene solution. After removal of solvents, a mixture (605 mg) was obtained that consisted of unchanged (1) (206 mg, 1.54 mmol) and *E*-(7) (399 mg, 2.10 mmol); yield based on unrecovered (1) 93%.

Reaction XV. Reactants: 2.200 g (0.93 mequiv. Br/g polymer; 2.05 mmol of functionality) of polymer (4; X = Br), 331 mg (2.47 mmol) of (1), benzene (40 ml), and 1.100 g (25 mmol) of ethylene oxide. Products: 2-(4-formylphenyl)-1,3-dioxolan, (14), m.p. 119–122 °C (209 mg, 1.17 mmol), mass spec.: M^+ , 177 ($M - 1$), 133 (base peak), n.m.r. (CCl₄): 0.05 (s, 1 H), 2.14, 2.28, 2.43, 2.57 (AA'BB' system, 4 H), 4.28 (s, 1 H), 6.08 (s, 4 H), and a mixture (230 mg; 1.10 mmol) of *Z*-(8) and *E*-(8); total yield 54% [total yield based on unacetalized (1) 85%].

Reaction XVI. Reactants: 5.162 g (0.55 mequiv. Cl/g polymer; 2.82 mmol of functionality) of polymer (4; X = Cl), 378 mg (2.82 mmol) of (1), and 2.0 g (44 mmol) of ethylene oxide. Products: mixture (285 mg) of *Z*-(8) (86 mg, 0.41 mmol) and *E*-(8) (199 mg, 0.96 mmol). Unchanged (1) (78 mg, 0.64 mmol) was recovered [total yield based on unchanged (1) 63%].

Reaction XVII. Reactants: 6.571 g (0.55 mequiv. Cl/g polymer; 3.56 mmol of functionality) of polymer (4; X = Cl), 238 mg (1.78 mmol) of (1) and 2.0 g (44 mmol) of ethylene oxide. Products: mixture (231 mg) of *p*-styrylbenzaldehydes (8) (160 mg, 0.77 mmol) and *p*-styrylstilbenes (12) (71 mg; 0.25 mmol); total yield 57%.

Reaction XVIII. Reactants: 1.000 g (0.93 mequiv. Br/g polymer; 0.93 mmol of functionality) of polymer (4; X = Br), 151 mg (1.13 mmol) of (2) and 1 g (22 mmol) of ethylene oxide. Products: mixture (129 mg, 0.62 mmol) of the *m*-styrylbenzaldehydes (17); unchanged (2) (30 mg, 0.22 mmol); and 2-(3-formylphenyl)-1,3-dioxolan (18) (14 mg, 0.08 mmol), mass spec.: M^+ , 177 ($M - 1$), 133 (base peak), n.m.r. (CCl₄): -0.05 (s, 1 H), 1.95–2.65 (complex absorption, 4 H), 4.13 (s, 1 H), 5.92 (s, 4 H); yield based on unrecovered (2) 68%.

Polymeric Procedure D Reactions.—These reactions were conducted as was reaction VI.

Reaction VII.^{1b} Reactants: 1.500 g (1.61 mequiv. P/g polymer; 2.42 mmol of functionality) of polymer (3), 942 mg (6.16 mmol) of methyl bromoacetate, 413 mg (3.08 mmol) of (1), and 2.0 g (44 mmol) of ethylene oxide. Products: mixture of 147 mg (1.10 mmol) of (1) and 369 mg (1.94 mmol) of *E*-(7); yield based on unrecovered (1) 98%.

Reaction VIII. Reactants: 1.500 g (2.05 mequiv. P/g polymer; 3.08 mmol of functionality) of polymer (3), 668 mg (6.16 mmol) of methyl chloroacetate, 413 mg (3.08 mmol) of (1) and 2.0 g (44 mmol) of ethylene oxide. Product: unchanged (1).

Reaction IX. Reactants: 1.500 g (1.49 mequiv. P/g polymer; 2.24 mmol of functionality) of polymer (3), 682 mg (4.46 mmol) of methyl bromoacetate, 292 mg (2.3 mmol) of (2) and 2.0 g (44 mmol) of ethylene oxide. Products: mixture (206 mg) consisting of 142 mg (1.06 mmol) of unchanged (2) and 64 mg (0.34 mmol) of methyl (*E*)-*m*-formylcinnamate, *E*-(16), n.m.r.: 0.00 (s, 1 H), 1.90–2.50 (complex absorption, 4 H), 2.62 (part A of an AB system, $J = 16$ Hz, 1 H), and 6.19 (s, 3 H).

[8/453 Received, 13th March, 1978]

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