Tetrahedron Vol 44, No 7, pp. 2049 to 2054, 1988
Printed in Great Britain

0040-4020/88 $3.00+.00
Pergamon Press plc

REGIOSPECIFIC FORMATION OF 1,3-DIENES BY THE PALLADIUM CATALYSED INTRA- AND INTER-MOLECULAR COUPLING OF VINYL HALIDES.[1]

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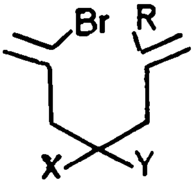
(*Received in UK* 29 *December* 1987)

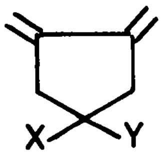
Abstract. Palladium acetate (5 mol %) effects catalytic inter- and intra-molecular coupling of vinyl bromides in good yield under mild conditions provided sufficient triarylphosphine and potassium carbonate are present to regenerate the active palladium(0) species. Wilkinson's catalyst is a poor catalyst for the same coupling reaction. Double bond isomerisation is not observed under these conditions. The palladium catalyst also couples iodobenzene to biphenyl in 48% yield whilst Wilkinson's catalyst is ineffective. The mechanism of the coupling process is discussed.

We recently reported the cyclisation of 2-bromo-1,6-dienes (1a) with $Pd(OAc)_2/2PPh_3$, $Pd(PPh_3)_4$ or $RhCl(PPh_3)_3$ in acetonitrile in the presence of potassium carbonate to give mixtures of cyclic dienes (2) and (3).[2] The rhodium catalyst showed good selectivity for (2) whilst the selectivity of palladium catalysts for (2) was greatly increased by the addition of tetraethyl ammonium chloride.[3] 2-Bromo-1,7-dienes are cyclised regiospecifically to 6-membered rings by the same metal catalysts but the cyclisation is accompanied by significant amounts of double bond isomerisation.[2]

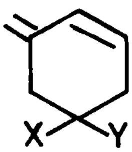
The problem of regioselectivity of the cyclisation process would be circumvented if a process for the catalytic coupling of vinyl halides was developed. Coupling of vinyl or aryl halides can be achieved by copper (Ullmann reaction)[4] but drastic conditions are often required. The coupling reaction using Ni(0) complexes discovered by Semmelhack[5] occurs under milder conditions and is particularly useful for intramolecular coupling. Other nickel[6] and cobalt[7] systems have been developed and a few examples of Pd(0) and Pt(0) complexes effecting aryl-aryl coupling have been reported.[8] We now report details of a palladium catalyst system capable of effecting inter- and intra-molecular coupling of certain vinyl bromides and, less effectively, aryl halides.



(1) a. R=H
b. R=Br,X=Y=CO_2Et



(2) a. X=Y=CO_2Et



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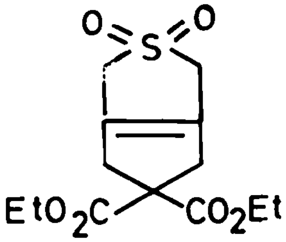


(4)

The 2,6-dibromohepta-1,6-diene (1b) is catalytically cyclised (MeCN, 80°C) to (2a) by 5 mole % palladium acetate in the presence of triarylphosphine and anhydrous potassium carbonate (table). The yield depends on both the concentration and nature of the triarylphosphine, with triphenylphosphine and $P(p\text{-}MeOC_6H_4)_3$ proving the most efficacious (table, entries 4 and 7). Diphos (table, entry 9) gave a very poor yield whilst triethylphosphite failed to effect any cyclisation.

Table. Effect of variation of quantity and nature of triarylphosphine on the cyclisation of (1b) to (2a).[a]

Entry	$Pd(OAc)_2$(mol %)	Ar_3P (mole %)	Time(h)	Yield(%)[b]
1	5	Ph_3P (50)	0.5	42[c]
2	10	Ph_3P (50)	1.0	50[c]
3	10	Ph_3P(75)	1.7	64[d]
4	5	Ph_3P(100)	3.5	92
5	5	Ph_3P(110)	2.5	80
6	5	Ph_3P(125)	1.25	82
7	5	$(p\text{-}MeOC_6H_4)_3P$(125)	1.25	90
8	5	$(p\text{-}FC_6H_4)_3P$(125)	1.25	75
9	5	diphos (125)	4.0	12[c]
10	5	Bu^n_3P (125)	33	50
11	5	$(o\text{-}MeC_6H_4)_3P$(125)	20	10[c]

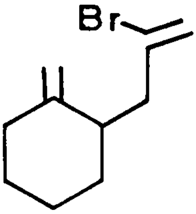
a. Reactions carried out at 80°C in acetonitrile in the presence of anhydrous potassium carbonate (2.5 equiv.).

b. Isolated yield.

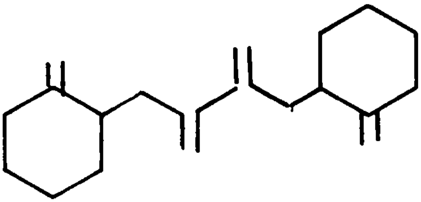
c. Estimated by g.l.c. (2m,SGR,190°C). Substantial amounts of starting material present.

d. Crude product contained 20% starting material.

Using 5 mol% catalyst, triphenylphosphine (1.25mol) and anhydrous potassium carbonate (2.5 equiv.) (MeCN, 80°C), palladium acetate effected faster cyclisation and gave a better yield than tetrakis(triphenylphosphine)Pd(0) and palladium chloride. Wilkinson's catalyst $[RhCl(Ph_3P)_3]$ (10 mol%) was less efficient than any of the palladium catalysts giving a 20% yield of (2a) after 58h. The diene (2a) reacts with liquid sulphur dioxide to give the cycloadduct (4) in 91% yield.



(5)



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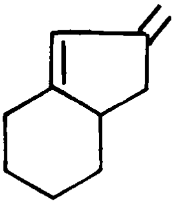

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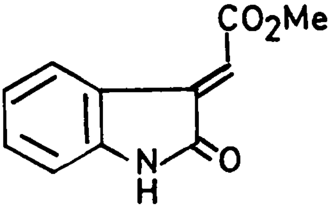
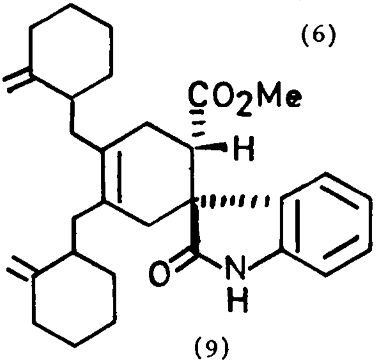
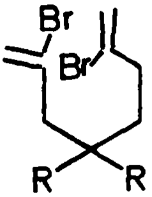


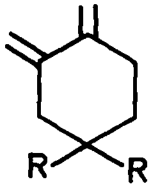
(8)



(9)



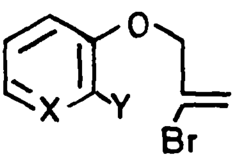
(10) R=CO$_2$Et



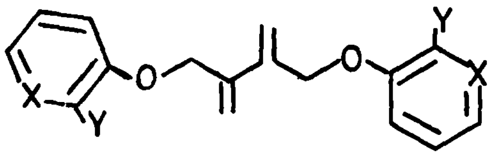
(11) R=CO$_2$Et

The vinyl bromide (5) was studied because it is potentially capable of undergoing an intramolecular Heck reaction[2] to give (6) or an intermolecular coupling to give the dimer (7). The sole product (90%) is (7) using 5 mol% palladium acetate, triphenylphosphine (50 mol%) and potassium carbonate (2.5 mol) (MeCN, 80^{o}C, 4.5h). Using Pd(Ph$_3$P)$_4$ as catalyst resulted in a longer reaction time (12h) and a reduced yield (70%) of (7) whilst Wilkinson's catalyst was much less effective in this reaction. As expected diene (7) undergoes the Diels-Alder reaction. Thus reaction of (7) with (8) (benzene, 80^{o}C, 48h) gives (9) (84%).

The cyclisation of the 2,7-dibromoocta-1,7-diene (10)→(11) can be achieved under analogous conditions to those developed for the cyclisation of (1b). However, the yield is low (28%) and the reaction is slow (14.5h). Attempts to extend the coupling process to aryl halides met with only moderate success. Bromobenzene failed to give any biphenyl whilst iodobenzene gave only a moderate yield (48%) even in n-butyl cyanide at 118^{o}C although all the iodobenzene was consumed. The by-product in these reactions is presumably tetraphenylphosphonium iodide.[9]



(12) a. X=CH, Y=H
b. X=CH, Y=Br
c. X=N, Y=Br



(13)

The greater reactivity of vinyl bromides compared to aryl bromides is illustrated by the palladium catalysed regiospecific intermolecular coupling of (12a-c) to (13a-c) in moderate yield (31-55%). Wilkinson's catalyst failed to effect these coupling reactions.

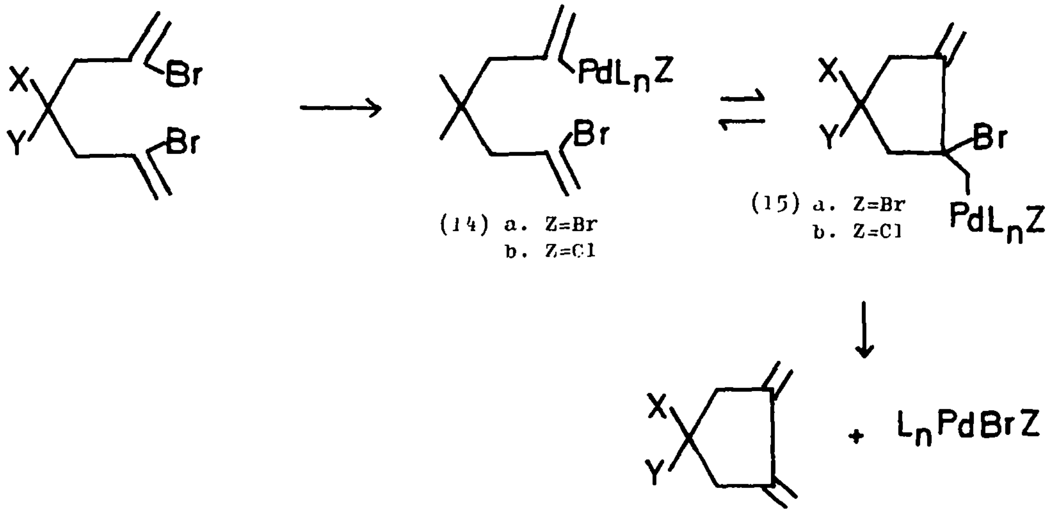
Mechanism of the coupling reaction

The mechanism of the coupling reaction is illustrated for the case of (1b) in the Scheme.

The mechanism [scheme, (a)] is analogous to that discussed previously for the intramolecular Heck reaction[2] except that the 5-exo-trig cyclisation of the vinylpalladium bromide is followed by elimination of palladium bromide rather than hydridopalladium bromide. Interestingly the addition of tetraethylammonium chloride (1 or 2 mol) to the palladium catalysed cyclisation of (1b) and lowering the reaction temperature to 30^{o}C failed to produce the marked rate accelerations noted previously for the intramolecular Heck reaction.[2] We suggested in this latter case that the tetraethylammonium chloride functioned as an anion exchange reagent (14a)→(14b), with the vinylpalladium chloride species (14b) promoting the 5-exo-trig cyclisation and/or the alkylpalladium chloride species (15b) promoting elimination of HPdCl. The lack of rate enhancement in the case of (1b) [scheme, (a)] could therefore be due to a lack of influence of chloride on the elimination of LnPdBrCl from (15b). However, it might also reflect a slower recycling of palladium chloride to palladium(0) [scheme, (b)] compared to palladium bromide.

The variation in yield of (2a) with the mol % of added phosphine (table) and the detection of triphenylphosphine oxide (g.l.c. and p.m.r.) accords with the proposed recycling mechanism [scheme, (b)].

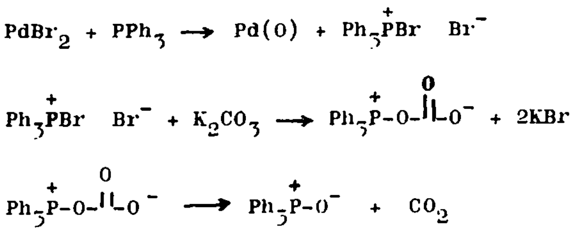
(a)



(14) a. Z=Br
b. Z=Cl

(15) a. Z=Br
b. Z=Cl

(b)



$$PdBr_2 + PPh_3 \longrightarrow Pd(0) + Ph_3\overset{+}{P}Br\ \ Br^-$$

$$Ph_3\overset{+}{P}Br\ \ Br^- + K_2CO_3 \longrightarrow Ph_3\overset{+}{P}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^- + 2KBr$$

$$Ph_3\overset{+}{P}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^- \longrightarrow Ph_3\overset{+}{P}\text{-}O^- + CO_2$$

SCHEME

Experimental

Experimental details were as previously noted.[2]

Vinyl Bromides

Diethyl di(2-bromoallyl)malonate, (1b). A mixture of diethyl malonate (11g, 6.9mmol), 2,3-dibromopropene (31g, 15.5mmol) and anhydrous potassium carbonate (21g, 15.5mmol) was boiled under reflux for 2d. The reaction mixture was then filtered and the filtrate concentrated and distilled to give the product (23.3g, 85%)as a colourless oil, b.p. 113-116°C/0.002mmHg (Found: C, 39.05; H, 4.55; Br, 39.85. $C_{13}H_{18}Br_2O_4$ requires C, 39.20; H, 4.55; Br, 40.15%); δ 5.7 and 5.6 (2 x 1H, 2 x d, 2 x CH_2=CBr), 4.2 (2 x 2H, q, 2 x CH_2Me), 3.3 (4H, s, 2 x CH_2CBr), and 1.3 (6H, t, 2 x MeCH_2); ν max(film) 3095, 2980, 2925, 2900, 2865, 1730, 1620, 1430, 1365, 1290, 1218, 900 and 855 cm^{-1}; m/z(%) 319(100), 314(97), 245(17), 243(17), 217(34), 215(36), 203(15), 201(14), 97(15), 91(49) and 43(83).

2-(2'-Bromoallyl)-methylenecyclohexane (4). A three-necked round bottomed flask (500ml) was fitted with a reflux condenser, a dropping funnel, a mechanical stirrer, and a gas inlet tube. A gentle flow of nitrogen was maintained throughout the reaction. A 1.45M ethereal solution of n-BuLi (29ml, 4.2mmol) and anhydrous ether (200ml) were added to the flask. The solution was stirred and triphenylmethyl phosphonium bromide (15g, 4.2mmol) was added cautiously over a 5 min period. The solution was stirred for 4h at room temperature and then freshly distilled 2-(2-'bromopropenyl)-cyclohexanone (10g, 4.6mmol) was added dropwise over 5 min. and the mixture was boiled under reflux overnight. The mixture was then allowed to cool to room temperature, filtered, the precipitate washed with ether (100ml) and the combined ether layers washed with water (100ml) until neutral, dried ($CaCl_2$) and concentrated to give a 1:1 mixture (9.4g) of starting material, and product. Recycling this mixture through the reaction a further two times afforded the product (6.4g, 64%) as a colourless oil b.p. 64°C/2mmHg (Found: C, 55.85; H, 7.05. $C_{10}H_{15}Br$ requires C, 55.85; H, 7.05%); δ 5.56 amd 5.44 (2 x 1H, 2 x d, CH_2=CBr), 4.69 and 4.57 (2 x 1H, 2 x s, CH_2=C), 2.69 (1H, m, 1H of CH_2CBr), 2.46 (2H, m, 1H of CH_2CBr and CHCH_2), 2.18 (2H, m, CH_2C=CH_2), and 1.47 (6H, m, $(CH_2)_3$); ν max(film) 3070, 2980, 2920, 2845, 1640, 1625, 1440, 1205 and 880 cm^{-1}; m/z(%) 135(100), 95(89), 93(38), 91(42), 79(48), 67(88), 55(39), 53(37), and 41(66).

Diethyl (2-bromobutenyl)malonate. A mixture of diethyl malonate (6.73g, 4.2mmol), 2,4-dibromobut-1-ene (8.78g, 4.1mmol), and anhydrous potassium carbonate (5.8g) in acetone (35ml) was boiled under reflux for 7d to give, after the usual work-up diethyl (2-bromobutenyl)malonate (6.0g, 50%), b.p. 122-4°C/1.7mmHg (Found: C, 45.00; H, 5.85. $C_{11}H_{17}BrO_4$ requires C, 45.05; H, 5.85%); δ 5.61 and 5.46 (2 x 1H, 1 x dd, CH_2=CBr), 4.22 (2 x 2H, q, 2 x Me$\underline{CH_2}$), 3.37 (1H, t, CH), 2.50 (2H, t, CH_2CBr), 2.17 (2H, q, CH_2), and 1.28 (2 x 3H, t, 2 x $\underline{Me}CH_2$); ν_{max}(film) 3090, 2970, 2930, 2900, 1725, 1625, 1425, 1370, 1340, 1035, 900 and 860 cm^{-1}; m/z(%) 294/292 (M^+,1), 214(20), 213(100), 183(22), 159(33), 141(15), and 140(10).

Diethyl (2-bromoallyl)-2'-bromobutenylmalonate (10). Diethyl (2-bromobutenyl) malonate (5.5g, 1.9mmol) was slowly added to a solution of sodium ethoxide [from sodium (0.52g, 2.3mmol)] in ethanol (55ml). The mixture was stirred for 15min, then 2,3-dibromopropene (4.65g, 2.3mmol) was slowly added and the reaction mixture boiled under reflux for 16h. Work-up afforded the product (5.1g, 65%) as a colourless oil b.p. 142-144°C/0.15mmHg (Found: C, 40.80; H, 5.00. $C_{11}H_{20}Br_2O_4$ requires C, 40.80; H, 4.90%); δ 5.69, 5.63 and 5.41 (1H, 2H, 1H, 3 x d, 2 x CH_2=CBr), 4.22 (2 x 2H, q, 2 x Me$\underline{CH_2}$), 3.17 (2H, d, CH_2CBr), 2.32 (4H, m, CH_2CH_2), and 1.28 (2 x 3H, t, $\underline{Me}CH_2$); ν_{max}(film) 3090, 2970, 2900, 1720, 1625, 1443, 1272, 1210, 1190, 1150, 1030, 895 and 860 cm^{-1}; m/z(%) 369(1), 367(2), 365(1), 333(64), 331(73), 280(14), 278(12), 215(20), 213(17), 199(51), 171(24), 153(44), 125(56), 65(34), and 43(38).

2'-Bromoallyl-2-bromophenyl ether (11b). a mixture of o-bromophenol (8g, 4.62mmol), 2,3-dibromopropene (12g, 5.0mmol) and anhydrous potassium carbonate (7g, 5.1mmol) in acetone (50ml) was boiled under reflux overnight and worked up in the usual way to give the product (10.5g, 78%) as a colourless liquid b.p. 94-97°C/0.5mmHg (Found: C, 37.10; H, 2.65. $C_9H_8Br_2O$ requires C, 37.00; H, 2.75%); δ 7.19 (4H, m, ArH), 6.12 and 5.70 (2 x 1H, 2 x m, CH_2=CBr), and 4.68 (2H, t, CH_2O); ν_{max}(film) 3090, 2970, 2870, 1650, 1590, 1580, 1483, 1447, 1280, 1250, 1230, 1060, 1035, 900, 847 and 750 cm^{-1}; m/z(%) 294/292 (M^+,4), 290(2), 204(30), 174(7), 172(7), 160(15), and 159(100).

2-Bromo-3-(2'-bromoallyl)pyridinyl ether (11c). A mixture of 2-bromo-3-pyridinol (15g, 8.6mmol), 2,3-dibromopropene (20g, 10mmol) and anhydrous potassium carbonate (15.8g, 10mmol) in acetone (200ml) was boiled under reflux overnight followed by work-up in the usual way to give the product (24.5g, 97%) which crystallised from methanol as pale yellow rods, m.p. 88-90°C (Found: C, 32.65; H, 2.40; N, 4.65; Br, 54.25. $C_8H_7Br_2NO$ requires C, 32.80; H, 2.40; N, 4.80; Br, 54.55%); δ 8.05 (1H, d, ArH), 7.19 (2H, m, ArH), 6.11 and 5.75 (2 x 1H, 2 x m, CH_2=CBr), and 4.73 (2H, t, CH_2O); ν_{max} 3097, 3030, 2900, 2840, 1625, 1560, 1445, 1420, 1410, 1375, 1290, 1205, 1080, 1050, 1020, 905, 795, 720, 705 and 690 cm^{-1}; m/z(%) 295(3), 293(7), 291(3), 205(32), 175(9), 173(9), 161(24), 160(100) and 91(22).

Coupling Reactions

Diethyl 3,4-bis(methylene)cyclopentane-1,1-dicarboxylate (2a). A mixture of diethyl di(2-bromoallyl)malonate, palladium acetate, triphenylphosphine and anhydrous potassium carbonate in acetonitrile (table) was boiled under reflux and monitored by g.l.c. (2m, 5% SGR, 190°C). When all the starting material had disappeared (table) the reaction mixture was worked up in the usual way to afford the product as a colourless oil, b.p. 55-68°C/0.5mmHg (molecular distillation) identical to that described previously.[2] δ 5.39 and 4.97 (2 x 2H, 2 x s, C=CH_2), 4.17 (4H, q, $\underline{CH_2}$Me), 3.03 (4H, s, CH_2), and 1.24 (6H, t, $CH_2\underline{Me}$).

Diels-Alder adduct (4). Diethyl 3,4-bis(methylene)cyclopentane-1,1-dicarboxylate (1.68g, 8.4mmol) was dissolved in liquid sulphur dioxide (10ml) and kept at 25°C for 2dy (sealed tube). The reaction mixture was then poured into 40-60° petroleum ether (50ml), the precipitated solid collected by filtration and crystallised from benzene to afford the product (1.92g, 91%) as pale yellow prisms, m.p. 90-91°C (Found: C, 51.40; H, 5.90. $C_{13}H_{18}O_6S$ requires C, 51.65; H, 6.00%); δ 4.21 (4H, q, $\underline{CH_2}$Me), 3.77 (4H, s), 3.14 (4H, s) and 1.27 (6H, t, $CH_2\underline{Me}$)

2,3-Bis(2-methylenecyclohexylmethyl)buta-1,3-diene (7). A mixture of 2(2'-bromoallyl)methylenecyclohexane (1.0g, 4.65 x 10^{-3}mol), palladium acetate (52mg, 2.32 x 10^{-4}mol), triphenylphosphine (609mg., 2.32 x 10^{-3}mol), and anhydrous potassium carbonate (1.6g, 1.16mmol) in acetonitrile (30ml) was boiled under reflux for 4.5h. Work-up in the usual way afforded the product (565mg, 90%), which distilled as a colourless oil, b.p. 30-50°C/0.05mmHg (molecular distillation) (Found: C, 88.85; H, 11.30. $C_{20}H_{30}$ requires C, 88.80; H, 11.20%); δ 5.08, 4.90, 4.66 and 4.57 (4 x 1H, 4 x d, C=CH_2), 2.34 (10H, m, CH_2C=C and CHCH_2), and 1.41 (6H, m, CH_2); ν_{max}(film) 3070, 2920, 2845, 1640, 1590, 1440 and 885 cm^{-1}; m/z(%) 270 (M^+,40), 175(53), 174(47), 161(45), 148(45), 147(30), 145(31), 135(73), 134(45), 133(64), 119(47), 95(100), 93(64), 91(93), 79(58) and 67(92).

Diels-Alder adduct (9). A mixture of 2,3-bis(2-methylenecyclohexylmethyl)buta-1,3-diene (70mg, 2.6 x 10^{-4}mol) and methyl 3-isatylidine acetate (50mg, 2.5 x 10^{-4}mol) in benzene (2ml) was boiled under reflux for 48h. The solvent was then removed and the residue crystallised from dichloromethane-hexane to afford the product (100mg, 84%), as colourless prisms m.p. 78-81°C (Found: C, 73.34; H, 7.20; N, 2.60. $C_{31}H_{39}O_3N.0.5CH_2Cl_2$ requires C, 73.30; H, 7.80;

N, 2.70%); δ 7.13 (4H, m, ArH), 4.64 (4H, m, CH_2=C), 3.50 (3H, s, OMe) and 1.94 (m, 27H, ring CH_2, CH_2C=C, CHC=C and $CHCO_2Me$).

Diethyl 3,4-bis(methylene)cyclohexane-1,1-dicarboxylate (11). A mixture of diethyl 2-bromoallyl-(2'-bromobutenyl)malonate (500mg, 1.2 x 10^{-3}mol), palladium acetate (14mg, 6 x 10^{-5}mol) and anhydrous potassium carbonate (400mg) in acetonitrile (20ml) was boiled under reflux for 14.5h whilst triphenylphosphine was added in four lots (2 x 130mg, 70mg and 35mg) at t=0,2,5 and 6h respectively. Work-up in the usual manner afforded the product (90mg, 28%) as a colourless oil, b.p. 30-50°C/0.01mmHg (molecular distillation), identical to that described previously.[2] δ 4.98, 4.91, 4.72 and 4.63 (4 x 1H, 4 x s, C=CH_2), 4.13 (4H, q, CH_2Me), 2.70 (2H, s, ring CH_2), 2.23 (2H, m, allylic CH_2), 2.08 (2H, t, ring CH_2), and 1.2 (6H, t, CH_2Me).

Biphenyl. A mixture of iodobenzene (340mg, 1.69 x 10^{-3}mol), palladium acetate (19mg, 8.4 x 10^{-4}mol), triphenylphosphine (267mg, 1.05 x 10^{-3}mol) and anhydrous potassium carbonate (500mg) in n-butyl cyanide was boiled under reflux for 80h, when g.l.c. (5% SGR, 2m, oven temp. 120°C) showed all the iodobenzene had been consumed and biphenyl (50%) (estimated using durene as an internal standard) had been formed.

2,3-Bis(phenoxymethyl)buta-1,3-diene (13a). A mixture of 2-bromoallyloxybenzene (500mg, 2.34 x 10^{-3}mol), $Pd(OAc)_2$ (26mg, 1.16 x 10^{-4}mol), triphenylphosphine (250mg, 9.5 x 10^{-4}mol) and anhydrous potassium carbonate (800mg) in acetonitrile (20ml) was boiled under reflux for 5h. Work-up followed by preparative t.l.c. (SiO_2) eluting with 4:1 v/v 40-60° petroleum ether-ether afforded the product (190mg, 31%) as a light yellow oil, b.p. 180-200°C/0.15mmHg (molecular distillation) (Found: C, 80.35; H, 6.50. $C_{18}H_{18}O_2$ requires C, 81.15; H, 6.80%); δ 7.04 (10H, m, ArH), 5.38 and 5.33 (2 x 2H, 2 x s, C=CH_2), and 4.66 (4H, s, CH_2O); ν_{max} 3040, 2910, 2860, 1635, 1600, 1590, 1490, 1220, 1210, 1032, 885, 740, and 675 cm^{-1}; m/z(%) 266 (M^+,10), 265(30), 190(100), 133(40), 94(27), 93(29), and 77(56).

2,3-Bis(2-bromophenoxymethyl)buta-1,3-diene (13b). Triphenylphosphine (125 mol%) was added in three portions (2 x 224mg, and 112mg) at t = 0, 0.35 and 0.70h to a mixture of (2'-bromoallyl) 2-bromophenyl ether (500mg, 1.71 x 10^{-3}mol), palladium acetate (19mg, 8.5 x 10^{-5}mol) and anhydrous potassium carbonate (550mg) in boiling acetonitrile. Heating was continued for a total of 1.15h. Work-up in the usual way followed by preparative t.l.c. (SiO_2) eluting with 4:1 v/v 40-60° afforded the product (225mg, 31%), as colourless plates from ether-chloroform, m.p. 46-47°C (Found: C, 50.95; H, 3.95. $C_{18}H_{16}Br_2O_2$ requires C, 50.95; H, 3.80%); δ 7.28 (8H, m, ArH), 4.75 (4H, s, CH_2O), and 4.68 and 4.09 (2 x 2H, 2 x d, C=CH_2); m/z(%) 386(5), 384(10), 382(5), 305(14), 303(15), 212(5), 211(8), 210(5), 132(77), and 131(100).

2,3-Bis(2-bromo-3-oxymethylpyridyl)buta-1,3-diene (13c). Triphenylphosphine (100 mol%), was added in three portions (2 x 280mg, and 140mg) at t = 0, 0.35 and 0.70h, to a mixture of 2'-bromoallyl 2-bromo-3-pyridimyl ether (750mg, 2.56 x 10^{-3}mol), tetrakistriphenylphosphine palladium(0) (148mg, 1.28 x 10^{-4}mol) and anhydrous potassium carbonate (800mg) in boiling acetonitrile (20ml). Heating was continued for a total of 1.5h. Work-up in the usual way afforded the product (602mg, 55%) as colourless plates from ether-chloroform, m.p. 109-111°C (Found: C, 44.85; H, 3.55; N, 6.50. $C_{16}H_{14}Br_2$ requires C, 45.10; H, 3.30; N, 6.55%); δ 8.26, 8.05, 7.53 (3 x 2H, 3 x m, PyH), 4.79 (6H, s + d, CH_2O and C=CHH) and 4.2 (d, 2H, C=CHH); ν_{max} 3040, 2920, 2840, 1660, 1555, 1410, 1300, 1275, 1205, 1085, 1057, 870, 800, 735, 725, and 690 cm^{-1}; m/z(%) 388(6), 386(13), 384(5), 307(34), 305(34), 214(82), 212(78), 133(100), 132(85) and 39(40).

We thank the Department of Education for Northern Ireland, S.E.R.C. and Queen's University for support.

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