

## Reactions of Azo and Azoxy Sulphones with Transition Metal Complexes. Part 7.<sup>1</sup> Arylation of Olefins with Arylazoxy Aryl Sulphones Catalysed by a Palladium(0) Phosphine Complex

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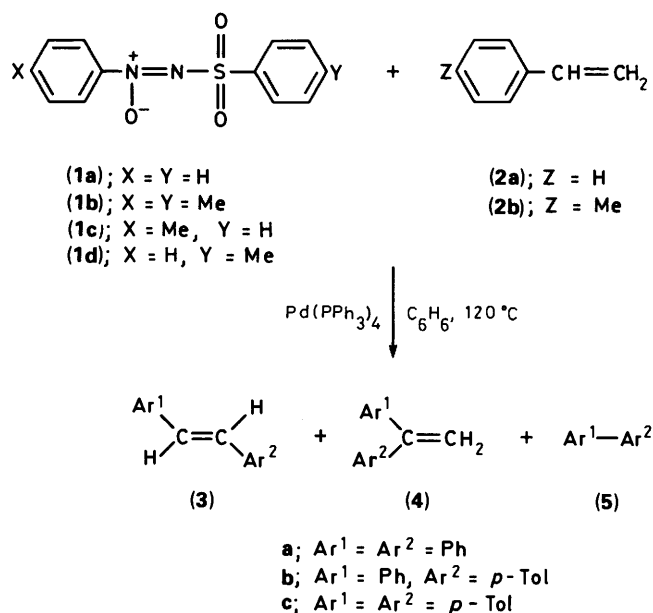
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The arylation of acyclic and cyclic olefins by arylazoxy aryl sulphones has been investigated in the presence of a palladium(0) catalyst in benzene. Both of the aryl groups of the arylazoxy aryl sulphones are found to participate in the arylation. Two equivalents of aryl-substituted olefins were obtained when the reactions were carried out at 80 °C, whereas one equivalent of olefin was arylated at 120 °C. A plausible catalytic cycle involving a diarylpalladium(II) species is proposed.

The arylation of unsaturated compounds by arenediazonium compounds in the presence of a copper salt, first disclosed by Meerwein, is a useful synthetic procedure for aryl olefins, though it has some limitations.<sup>2</sup> Many papers have since reported modified Meerwein arylations with significant improvements.<sup>3-5</sup> Recently we reported that reaction of arylazo aryl sulphones with olefins, catalysed by a palladium(0) complex, gives aryl-substituted olefins in good yields.<sup>6</sup> A characteristic feature of this reaction is that either of the aryl groups of the arylazo aryl sulphone is incorporated in the product olefin and the other aryl group leaves as an arene. Accordingly, only one aryl group of the arylazo aryl sulphone acts as the arylating group. During our studies on the arylation of olefins by arylazo compounds, we found that arylazoxy aryl sulphones† arylate two equivalents of olefins in the presence of a palladium(0) phosphine complex to give the corresponding aryl-substituted olefins in high yield. In this case both aryl groups of the arylazoxy aryl sulphones therefore act as the arylating reagent.

The reaction of phenylazoxy phenyl sulphone (**1a**) (1.0 mmol) with styrene (**2a**) (5.0 mmol) proceeds very smoothly in the presence of catalytic tetrakis(triphenylphosphine)palladium(0) in benzene in a degassed sealed tube at 120 °C for 24 h, to give (*E*)-stilbene (**3a**) (0.77 mmol), 1,1-diphenylethylene (**4a**) (0.05 mmol), and biphenyl (**5a**) (0.08 mmol). The reaction appears to be catalysed by the palladium(0) complex since arylazoxy aryl sulphones (**1**) are thermally very stable compounds.‡ Several other transition metal catalysts, such as Pd(dba)<sub>2</sub>, Pd(dba)<sub>2</sub> + PPh<sub>3</sub>, PdCl<sub>2</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>, PdCl<sub>2</sub>(PhCN)<sub>2</sub>, Pd(OAc)<sub>2</sub>, NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, RhCl(PPh<sub>3</sub>)<sub>3</sub>, and RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, were employed for the reaction of (**1a**) with styrene under similar conditions, but showed low catalytic effect to give the products (**3a**), (**4a**), and (**5a**) only in low yields, with high recovery of unchanged (**1a**).

The reaction of (**1a**) with styrene gave selectively the β-substituted styrene (**3a**), with the α-substituted product (**4a**) as a minor product. The selectivity for the β-position is much higher



than that for the phenylation of styrene with phenylazo phenyl sulphone ( $\alpha:\beta = 1:3$ ).<sup>6</sup>

Similarly, reaction of *p*-tolylazoxy *p*-tolyl sulphone (**1b**), phenyl *p*-tolylazoxy sulphone (**1c**), or phenylazoxy *p*-tolyl sulphone (**1d**) with styrene or *p*-methylstyrene (**2b**) was carried out in the presence of tetrakis(triphenylphosphine)palladium(0) in benzene in a degassed sealed tube at 120 °C. The results are summarized in Table 1.

The reactions of the azoxy sulphone (**1a**) with *p*-methylstyrene (**2b**) and of (**1b**) with (**2a,b**) gave the corresponding β- and α-arylated styrenes, (**3**) and (**4**) respectively, in high yield with a similar product distribution to that observed in the reaction of (**1a**) with styrene. The reaction of (**1c**) (1 mmol) with styrene gave (*E*)-stilbene (**3a**) (0.48 mmol), (*E*)-1-phenyl-2-(*p*-tolyl)ethylene (**3b**) (0.49 mmol), 1,1-diphenylethylene (**4a**) (0.05 mmol), 1-phenyl-1-(*p*-tolyl)ethylene (**4b**) (0.07 mmol), and *p*-methylbiphenyl (**5b**) (0.07 mmol); a similar result was obtained in the reaction of (**1d**) with styrene. It is of interest that the product ratios of (**3a**):(**3b**) and (**4a**):(**4b**) were almost equal in the reactions of (**1c**) and (**1d**) with styrene. These results show that either of the two aryl groups in (**1**) can arylate styrenes at the α- and β-positions in almost the same amount and suggest

† Arylazoxy aryl sulphones (**1**) are *N*-oxide derivatives of the corresponding arylazo aryl sulphones. There are only a few reports on the preparations and reactions of (**1**),<sup>7</sup> and there is no report on the arylation of olefins with (**1**).

‡ When phenylazoxy *p*-tolyl sulphone (**1c**) was refluxed in nitrobenzene (210 °C) for 3 days ca. 60% of (**1c**) was consumed, and 10% of nitrobiphenyl (isomeric distributions: *ortho* 49%, *meta* 14%, and *para* 37%), 14% of toluene-*p*-sulphonic acid, and a trace amount of azobenzene were obtained.



**Table 1.** Arylation of styrenes with arylazoxy aryl sulphones (1) catalysed by Pd(PPh<sub>3</sub>)<sub>4</sub> at 120 °C<sup>a</sup>

Entry	Azoxy sulphone	Styrene	Products (yields, <sup>b</sup> mol/mol azoxy sulphone)	Total yield (mol/mol azoxy sulphone)
1	(1a)	(2a)	(3a) (0.77) and (4a) (0.05)	0.82
2	(1a)	(2b)	(3b) (0.80) and (4b) (0.11)	0.91
3	(1b)	(2a)	(3b) (0.83) and (4b) (0.12)	0.95
4	(1b)	(2b)	(3c) (0.97) and (4c) (0.19)	1.16
5	(1c)	(2a)	(3a) (0.48), (3b) (0.49), (4a) (0.05), and (4b) (0.07)	1.09
6	(1d)	(2a)	(3a) (0.30), (3b) (0.26), (4a) (0.05), and (4b) (0.04)	0.65

<sup>a</sup> All reactions were performed with 1 mmol of arylazoxy aryl sulphone (1), 5 mmol of styrene, and 0.01 mmol of tetrakis(triphenylphosphine)palladium(0) in benzene (5 ml) in a degassed sealed tube at 120 °C for 24 h. <sup>b</sup> Yields were determined by g.l.c. based on the arylazoxy aryl sulphone used. Biaryl (Ar<sup>1</sup>Ar<sup>2</sup>) was formed in 0.03–0.07 mol/mol azoxy sulphone in all the reactions.

**Table 2.** Arylation of styrenes with arylazoxy aryl sulphones (1) catalysed by Pd(PPh<sub>3</sub>)<sub>4</sub> at 80 °C<sup>a</sup>

Entry	Azoxy sulphone	Styrene	Products (yields, <sup>b</sup> mol/mol azoxy sulphone)	Total yield (mol/mol azoxy sulphone)
1	(1a)	(2a)	(3a) (1.35) and (4a) (0.20)	1.55
2	(1a)	(2b)	(3b) (1.31) and (4b) (0.24)	1.55
3	(1b)	(2a)	(3b) (1.52) and (4b) (0.22)	1.74
4	(1b)	(2b)	(3c) (1.36) and (4c) (0.29)	1.65
5	(1c)	(2a)	(3a) (0.78), (3b) (0.76), (4a) (0.11), and (4b) (0.15)	1.80
6	(1d)	(2a)	(3a) (0.67), (3b) (0.76), (4a) (0.09), and (4b) (0.10)	1.62

<sup>a</sup> All reactions were carried out with 1 mmol of arylazoxy aryl sulphone (1), 5.0 mmol of styrene, and 0.01 mmol of the palladium(0) catalyst in benzene (5 ml) in a degassed sealed tube at 80 °C for 24 h. <sup>b</sup> Yields were determined by g.l.c. based on the arylazoxy aryl sulphone (1) used. Biaryl (Ar<sup>1</sup>Ar<sup>2</sup>) was formed in 0.03–0.05 mol/mol azoxy sulphone in all the reactions.

**Table 3.** Arylation of styrenes with (1) catalysed by palladium(0) complex<sup>a</sup>

Arylazoxy arylsulphone	Alkene	Reaction temp. (°C)	Products (yields mol/mol azoxy sulphone)
(1a)	(2a)	80	(6a) (0.70), (3a) (0.02), and (4a) (0.00)
(1b)	(2b)	80	(6b) (0.65), (3b) (0.13), and (4b) (0.03)
(1a)	(2a)	120	(6a) (0.00), (3a) (0.52), and (4a) (0.00)
(1b)	(2b)	120	(6b) (0.08), (3b) (0.53), and (4b) (0.04)

<sup>a</sup> All reactions were carried out in a degassed sealed tube using 1.0 mmol of (1) and 1.0 mmol of an alkene in the presence of a catalytic amount of the palladium(0) complex.

that a common reactive intermediate, in which both aryl groups have same reactivity towards the olefin, is formed from both (1c) and (1d) by the palladium(0) catalysed reaction.

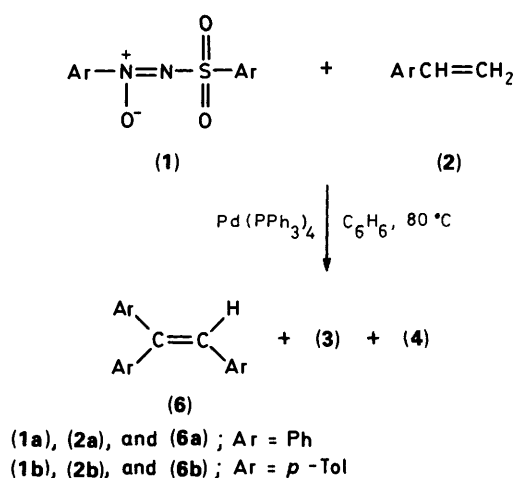
The total yields of (3), (4), and (5) in the reactions of (1b) with *p*-methylstyrene and (1c) with styrene exceeded 1.0 mol/mol azoxy sulphone (Table 1, entries 4 and 5, respectively). We considered that these results are not due to experimental error, but suggest that both aryl groups of the arylazoxy aryl sulphones participate in the arylation reactions; hence the maximum possible yield is 2.0 mol/mol azoxy sulphone. By examining the reaction conditions it was hoped to approach this. Thus, the reaction of (1a) (1 mmol) with styrene (5 equiv.) was studied in the presence of palladium(0) complex under milder conditions (80 °C) in a degassed sealed tube. As expected, the yields of (3a), (4a), and (5a) increased to 1.35, 0.20, and 0.05 mmol, respectively, and the total yield increased to 1.60 mol/mol azoxy sulphone. Similarly, other reactions of (1) with styrenes in the presence of palladium(0) complex were carried out at 80 °C, and the total yields of (3), (4), and (5) were 1.60–1.85 mol/mol azoxy sulphone as shown in Table 2. The results support our idea that the two aryl groups of (1) participate in the arylation of olefins under milder reaction conditions.

The reaction of (1a) with one equivalent of styrene was carried out in the presence of the palladium(0) catalyst at 80 °C.

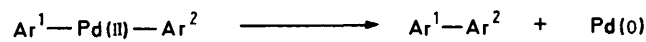
In this case, styrene was doubly phenylated, and triphenylethylene (6a) and (3a) were obtained in 0.70 and 0.02 mol/mol azoxy sulphone yield, respectively. Similarly, reaction of (1b) with one equivalent of *p*-methylstyrene in the presence of the palladium(0) catalyst at 80 °C afforded tri(*p*-tolyl)ethylene (6b) as the major product together with (3c) (0.13 mol/mol azoxy sulphone) and (4c) (0.03 mol/mol azoxy sulphone). However, reaction of (1a) or (1b) with one equivalent of styrene or *p*-methylstyrene, respectively, at 120 °C gave (3a) (0.52 mol/mol azoxy sulphone) or (3c) (0.53 mol/mol azoxy sulphone) as the major product, with (6) and (4) as minor products. The results are summarized in Table 3. The tri-arylethylenes are considered to be formed by the stepwise arylation of the starting vinylarene to give initially a 1,1- or 1,2-diarylethylene which is then further arylated. These results also support the double arylation of olefins by (1) at 80 °C.

A plausible catalytic cycle for this reaction is outlined in Scheme 1. Oxidative addition of (1) to the palladium(0) catalyst gives the adduct (7) which loses nitrous oxide and sulphur dioxide to give the diarylpalladium(II) species (8). Subsequent addition of (8) to the olefin gives the adduct (9) from which elimination of an arylpalladium group and  $\beta$ -hydrogen gives the aryl-substituted olefins (3) and (4) and the arylhydrogen-palladium(II) (10). The intermediate (10) reacts with a further

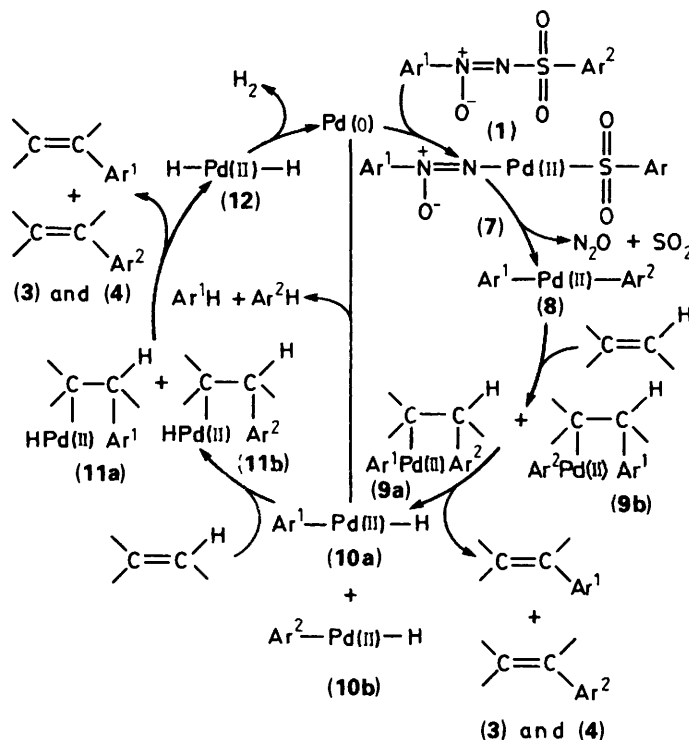




and  $\text{Ar}^2\text{SO}_2\text{Pd}(\text{II})\text{H}$  [or  $\text{Ar}^1\text{N}^+(\text{O}^-)\text{NPd}(\text{II})\text{H}$ ], which then degrade to  $\text{Ar}^2\text{SO}_2\text{H}$  [or  $\text{Ar}^1\text{N}^+(\text{O}^-)\text{NH}$ ] and palladium(0) are considered unlikely. In the reaction of (1) at  $120^\circ\text{C}$ , the arene is formed by reductive elimination from (10) and palladium(0) is regenerated. The differences in the reaction yields at 120 and  $80^\circ\text{C}$  can therefore be attributed to the preferential elimination of arene from the intermediate (10) at  $120^\circ\text{C}$ , but preferential addition of olefin at  $80^\circ\text{C}$ .<sup>\*</sup> Presumably, (10) is less stable at  $120^\circ\text{C}$  and hence will decompose to arene at this temperature rather than add to olefins. The formation of biaryl, which was observed in all reactions of (1) in 0.05–0.08 mol/mol azoxy sulphone yield, is accounted for by the reductive elimination of biaryl ( $\text{Ar}^1\text{Ar}^2$ ) from the intermediate (8).



The reactions of (1) with cycloalkenes were also carried out



molecule of olefin to give the aryl-substituted olefin and dihydrogenpalladium(II) (12) via the adduct (11). The palladium(0) catalyst is regenerated by reductive elimination of hydrogen.

The formation of nitrous oxide and sulphur dioxide was detected by mass spectroscopy although hydrogen could not be confirmed. There is a possibility of the formation of ethylbenzene by the reduction of styrene with the dihydrogenpalladium(II) species (12)—however, this was not detected from the reaction mixture of (1a) with styrene by capillary g.c. or g.c.-m.s. When the reaction of phenyl *p*-tolylazoxy sulphone (1c) (1 mmol) with styrene, catalysed by palladium(0) at  $80^\circ\text{C}$ , was stopped after 1.5 h, 16% of (1c) was consumed, and (3a) (0.065 mmol), (3b) (0.065 mmol), (4a) (0.015 mmol), and (4b) (0.014 mmol) were formed. These results, showing that the product ratios (3a):(3b) and (4a):(4b) are also equal in the initial reaction stage, suggests that the diarylpalladium(II) species (8) is a likely intermediate. The alternative mechanisms, which involve reaction of  $\text{Ar}^1\text{Pd}(\text{II})\text{SO}_2\text{Ar}^2$  [or  $\text{Ar}^1\text{N}^+(\text{O}^-)\text{NPd}(\text{II})\text{Ar}^2$ ] and the olefin to give the aryl-substituted olefin

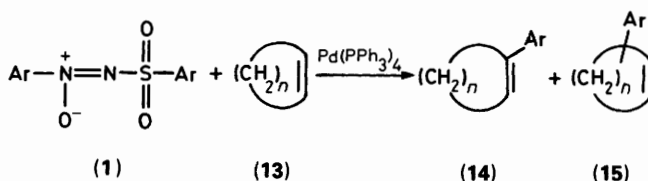
at 120 and  $80^\circ\text{C}$ . In this case, mixtures of 3- and 4- and/or 5-arylcycloalkenes were formed as major products, and 1-arylcycloalkenes as minor products. The results are summarized in Table 4. Large differences in the total yield of the arylation products were also found between the reactions of (1) at 120 and  $80^\circ\text{C}$ . The formation of 4- and/or 5-arylcycloalkenes may be accounted for by the palladium(0)-catalysed isomerization of the initial 1- and/or 3-arylcycloalkenes, as reported by Kikukawa *et al.*<sup>8</sup>

<sup>\*</sup> We assumed a diarylpalladium(II) intermediate  $[\text{Ar}^1\text{Pd}(\text{II})\text{Ar}^2]$  in the reaction of arylazo aryl sulphone catalysed by a palladium(0) complex.<sup>6</sup> In this case, either aryl group ( $\text{Ar}^1$  or  $\text{Ar}^2$ ) was involved in the arylation of olefins. However, both aryl groups of the azoxysulphone ( $\text{Ar}^1$  and  $\text{Ar}^2$ ) were found to add to the olefin, although the same diarylpalladium(II) species  $[\text{Ar}^1\text{Pd}(\text{II})\text{Ar}^2]$  is also proposed. These differences may be accounted as follows: in the reactions of azoxy-sulphones, the process from (10) to Pd(0) via (11) and (12) are probably made easier by the oxidative participation of nitrous oxide formed in a previous step.



**Table 4.** Arylation of cycloalkenes with (1) catalysed by palladium(0) complex

Arylazoxy aryl sulphone	<i>n</i> in (13)	Reaction temp. (°C)	Products, yields (mol/mol azoxy sulphone)		Total yield (mol/mol azoxy sulphone)
			(14)	(15)	
(1a)	3	120	0.02	0.35	0.37
(1a)	3	80	0.18	1.37	1.55
(1b)	3	120	0.03	0.27	0.30
(1b)	3	80	0.40	1.20	1.60
(1a)	4	120	0.19	0.34	0.53
(1a)	4	80	0.07	0.76	0.83
(1b)	4	120	0.06	0.25	0.31
(1b)	4	80	0.06	0.68	0.74
(1a)	5	120	0.00	0.72	0.72
(1a)	5	80	0.07	1.37	1.44
(1b)	5	120	0.03	0.70	0.73
(1b)	5	80	0.05	1.40	1.45
(1a)	6	120	0.10	0.58	0.68
(1a)	6	80	0.19	1.28	1.47
(1b)	6	120	0.05	0.39	0.44
(1b)	6	80	0.10	1.25	1.35



### Experimental

I.r. spectra were determined on a Hitachi 260-10 spectrometer with samples as either neat liquids or KBr discs.  $^1\text{H}$  N.m.r. spectra were measured on a JEOL JNM-PMX 60SI (60 MHz) spectrometer.  $^{13}\text{C}$  N.m.r. spectra were measured on a JEOL JNM Fx90Q FT n.m.r. (90 MHz) spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. signals were referenced to  $\text{Me}_4\text{Si}$  as an internal standard. Mass spectra were measured on a JEOL JMS DX-300 spectrometer by electron impact (e.i.) ionizing technique at 70 eV. Gas chromatography was performed by using a Hitachi 263-30 gas chromatograph with SE-30 (10%) 1 m stainless column. Gel-permeation chromatography was performed using a JAI LC-008 liquid chromatograph with JAIGEL-1H column (20 × 600 mm × 2) using chloroform as eluant.

All solvents were distilled and stored under nitrogen. Palladium chloride (Wako Chemicals) was used without further purification. Tetrakis(triphenylphosphine)palladium(0),<sup>9</sup> bis(dibenzylideneacetone)palladium(0),<sup>10</sup> palladium acetate(II),<sup>11</sup> dichlorobis(triphenylphosphine)palladium(II),<sup>12</sup> dichlorobis(acetonitrile)palladium(II),<sup>13</sup> dichlorobis(benzonitrile)palladium(II),<sup>13</sup> dichlorotris(triphenylphosphine)ruthenium(II),<sup>14</sup> dichlorobis(triphenylphosphine)nickel(II),<sup>15</sup> and chlorotris(triphenylphosphine)rhodium(I),<sup>16</sup> were prepared by the methods described in the literature. Phenylazoxy phenyl sulphone (1a), m.p. 119–121 °C (lit.,<sup>17</sup> 123 °C), *p*-tolylazoxy *p*-tolyl sulphone (1b), m.p. 102–104 °C (lit.,<sup>17</sup> 106 °C), phenyl *p*-tolylazoxy sulphone (1c), m.p. 80–82 °C, and phenylazoxy *p*-tolyl sulphone (1d), m.p. 109–110 °C (lit.,<sup>17</sup> 112–113 °C) were prepared by the published procedures.<sup>17</sup> Alkenes (Tokyo Kasei Chemicals) were purified by distillation prior to use.

**General Procedure for the Reaction of Arylazoxy Aryl Sulphones (1) with Alkenes.**—A solution containing (1) (1.0 mmol), alkene (5.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.01 mmol) in dry benzene (5 ml) was degassed by

a freeze-thaw cycle, sealed in an ampoule and heated at 80 °C or 120 °C for 24 h. The reaction mixture was subjected to short column chromatography on Florisil using benzene as eluant to remove the metal complex. The yields of the products were determined by g.c. using eicosane, dibenzyl, and (*E*)-stilbene as the internal standards. The products were isolated from the reaction mixture by the use of gel-permeation chromatography and/or column chromatography over silica gel (Wakogel C-60) and identified by i.r., n.m.r., and m.s. The structures of (*E*)-stilbene (3a), 1,1-diphenylethylene (4a), biphenyl (5a), 4-methylbiphenyl (5b), 4,4'-dimethylbiphenyl (5c), 1-phenylcyclohexene, and triphenylethylene (6a) were identified by comparison of their retention times on g.c., and their i.r.,  $^1\text{H}$  n.m.r., and g.c. mass spectral data with those of authentic samples. Phenylcycloheptenes [ $m/z$  172 ( $M^+$ )], (*p*-tolyl)cycloheptenes [ $m/z$  186 ( $M^+$ )], phenylcyclo-octenes [ $m/z$  186 ( $M^+$ )], and (*p*-tolyl)cyclo-octenes [ $m/z$  200 ( $M^+$ )] were determined only by the retention times of g.c. and g.c. mass spectra compared with those of authentic samples. The structures of the following products were determined by their i.r.,  $^1\text{H}$  n.m.r., and m.s. spectra:

(*E*)-1-Phenyl-2-(*p*-tolyl)ethylene (3b): m.p. 116–117 °C (lit.,<sup>18</sup> 119–120 °C);  $\nu_{\text{max}}$  (KBr) 3 030, 1 600, 1 510, and 1 450  $\text{cm}^{-1}$ ;  $\delta$ ( $\text{CDCl}_3$ ) 2.33 (3 H, s) and 6.83–7.60 (11 H, m);  $m/z$  194 ( $M^+$ ).

(*E*)-1,2-Di(*p*-tolyl)ethylene (3c): m.p. 182–183 °C (lit.,<sup>19</sup> 179–180 °C);  $\nu_{\text{max}}$  (KBr) 3 030, 2 920, and 1 510  $\text{cm}^{-1}$ ;  $\delta$ ( $\text{CDCl}_3$ ) 2.33 (6 H, s) and 6.93–7.40 (10 H, m);  $m/z$  208 ( $M^+$ ).

1-Phenyl-1-(*p*-tolyl)ethylene (4b):<sup>20</sup> Colourless oil;  $\nu_{\text{max}}$  (neat) 3 020, 2 920, 1 600, 1 510, 1 490, and 1 440  $\text{cm}^{-1}$ ;  $\delta$ ( $\text{CDCl}_3$ ) 2.30 (3 H, s), 5.35 (2 H, s), and 6.88–7.40 (9 H, m);  $m/z$  194 ( $M^+$ ).

1,1-Di(*p*-tolyl)ethylene (4c):<sup>21</sup> Colourless oil;  $\nu_{\text{max}}$  (neat) 3 020, 2 910, 1 600, and 1 510  $\text{cm}^{-1}$ ;  $\delta$ ( $\text{CDCl}_3$ ) 2.33 (6 H, s), 5.30 (2 H, s), and 6.90–7.23 (8 H, m);  $m/z$  208 ( $M^+$ ).

Tri(*p*-tolyl)ethylene (6b):<sup>22</sup>  $\nu_{\text{max}}$  (neat) 3 030, 2 920, 1 520, and 1 450  $\text{cm}^{-1}$ ;  $\delta$ ( $\text{CDCl}_3$ ) 2.18–2.30 (9 H, m) and 6.70–7.25 (13 H, m);  $m/z$  298 ( $M^+$ ).

1-Phenylcyclopentene:<sup>23</sup> Colourless oil;  $\nu_{\text{max}}$  (neat) 2 940, 1 740, 1 600, 1 490, and 1 440  $\text{cm}^{-1}$ ;  $\delta$ ( $\text{CDCl}_3$ ) 1.60–2.90 (6 H, m), 5.93–6.23 (1 H, m), and 6.83–7.60 (5 H, m);  $m/z$  144 ( $M^+$ , 100%), 129(91), 115(48), and 91(13).

3-Phenylcyclopentene:<sup>24</sup> Colourless oil;  $\nu_{\text{max}}$  (neat) 3 060,



2 940, 2 850, 1 600, 1 490, and 1 450  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.27–2.67 (4 H, m), 3.60–4.07 (1 H, m), 5.50–6.00 (2 H, m), and 6.83–7.33 (5 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  32.5, 33.8, 51.4, 126.0, 127.2, 128.4, 131.9, 134.3, and 146.5;  $m/z$  144 ( $M^+$ , 100%), 129(96), 115(30), 91(14), and 83(41).

1-(*p*-Tolyl)cyclopentene:<sup>23,25</sup> Colourless oil;  $\nu_{\text{max}}(\text{neat})$  2 930, 1 730, 1 680, and 1 600  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  1.60–2.87 (9 H, m), 5.90–6.13 (1 H, m), and 6.98 and 7.19 (4 H, ABq,  $J$  8.4 Hz);  $m/z$  158 ( $M^+$ , 43%), 156(100), 143(79), and 128(46).

3-(*p*-Tolyl)cyclopentene:<sup>6</sup> Colourless oil;  $\nu_{\text{max}}(\text{neat})$  2 920, 1 670, 1 610, and 1 510  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.10–4.07 (8 H, m), 5.50–5.97 (2 H, m), and 6.93 (4 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  20.9, 32.5, 33.9, 51.0, 126.8, 127.1, 129.0, 131.6, 134.5, and 143.5;  $m/z$  158 ( $M^+$ , 53%), 143(100).

3-Phenylcyclohexene:<sup>26</sup> Colourless oil;  $\nu_{\text{max}}$  2 930, 1 675, and 1 445  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.30–2.38 (6 H, m), 3.18–3.63 (1 H, m), 5.63–5.90 (2 H, m), and 7.15 (5 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.2, 25.1, 32.6, 41.9, 126.0, 126.9, 127.7, 128.3, 130.2, and 146.7;  $m/z$  158 ( $M^+$ ).

4-Phenylcyclohexene:<sup>27</sup> Colourless oil;  $\nu_{\text{max}}(\text{neat})$  3 020, 2 900, 1 660, 1 458, and 1 445  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.23–2.37 (6 H, m), 2.50–3.07 (1 H, m), 5.61 and 5.73 (2 H, ABq,  $J$  13.2 Hz), and 7.10 (5 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  25.9, 29.8, 33.4, 40.2, 126.0, 126.9, 127.0, 128.4, and 147.4;  $m/z$  158 ( $M^+$ ).

1-(*p*-Tolyl)cyclohexene:<sup>28</sup> Colourless oil;  $\nu_{\text{max}}(\text{neat})$  2 920, 1 510, and 1 450  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  1.30–2.50 (11 H, m), 5.70–6.10 (1 H, m), and 6.96 and 7.10 (4 H, ABq,  $J$  8.4 Hz);  $m/z$  172 ( $M^+$ , 100%), 157(71), 144(35), and 129(90).

3-(*p*-Tolyl)cyclohexene:<sup>6</sup> Colourless oil;  $\nu_{\text{max}}(\text{neat})$  2 920, 1 649, 1 510, and 1 450  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  1.17–2.47 (9 H, m), 3.10–3.57 (1 H, m), 5.30–6.07 (2 H, m), and 7.00 (4 H, s);  $m/z$  172 ( $M^+$ , 100%), 157(79), 144(31), 129(86), 115(26), and 105(30).

4-(*p*-Tolyl)cyclohexene: Colourless oil;  $\nu_{\text{max}}(\text{neat})$  3 020, 2 910, 1 650, 1 510, and 1 430  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  1.40–3.05 (10 H, m), 5.40–5.95 (2 H, m), and 7.00 (4 H, s);  $m/z$  172 ( $M^+$ , 100%), 157(77), 144(33), 129(94), 115(37), and 105(52) (Found:  $M^+$ , 172.1288.  $\text{C}_{13}\text{H}_{16}$  requires  $M$ , 172.1252).

1-(*p*-Tolyl)cyclo-octene:<sup>29</sup> Colourless oil;  $\nu_{\text{max}}(\text{neat})$  2 920, 1 640, 1 470, and 1 440  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  1.20–2.87 (15 H, m), 5.86 (1 H, t,  $J$  7.2 Hz), and 6.83–7.37 (4 H, m);  $m/z$  200 ( $M^+$ , 41%), 185(24), 172(100), 157(46), 143(54), and 132(87).

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