Palladium-catalysed 1,4-Arylation/Alkylation of Buta-1,3-diene with Halogenoarenes and Stabilised Anions[1]

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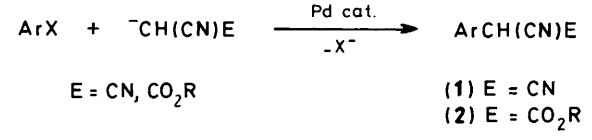
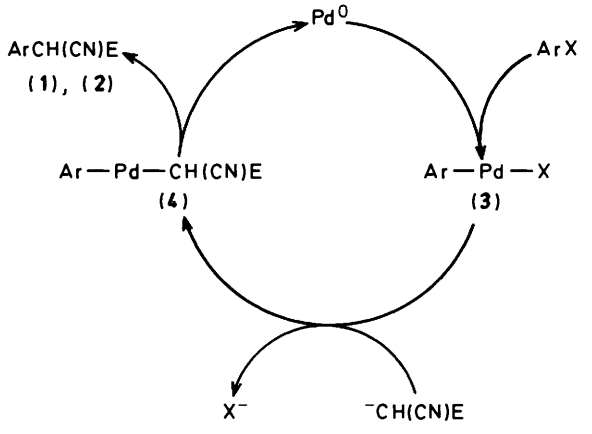
In the presence of a palladium–phosphine catalyst, buta-1,3-diene reacts with halogenoarenes and $^-CH(CN)_2$ to give 1,4-arylation/alkylation products of the diene, $ArCH_2CH{=}CHCH_2C(Ar)(CN)_2$ (**6**), in moderate yields. In this reaction, two carbon–carbon bonds are built up from three components by a tandem insertion/coupling reaction in one catalytic cycle. Stabilised anions such as $^-CH(CN)CO_2Me$ and $^-CH(CO_2Et)_2$ similarly yield 1,4-arylation/alkylation products.

Recently carbon–carbon bond formation catalysed by transition-metal complexes has been used extensively in organic syntheses.[2] In such reactions, π-allylmetal complexes frequently play an important role in carbon–carbon bond formation because of their high reactivities toward various nucleophiles which results in transfer of the allyl group from the metal to the nucleophile. π-Allylpalladium chemistry has been particularly well-developed by Tsuji and Trost for the syntheses of various organic compounds including natural products, in which a carbon–carbon bond formation is accomplished in a catalytic system *via* π-allylpalladium intermediates, starting from allyl acetates or allylcarbonates.[3] On the other hand, 1,3-dienes insert into a metal–carbon bond and easily form π-allylmetal species.[4] Thus, the insertion reaction of a 1,3-diene constitute one method for the preparation of π-allylpalladium complexes.

Previously we have shown that stabilised anions such as $^-CH(CN)_2$ and $^-CH(CN)CO_2R$ smoothly react with halogenoarenes in the presence of a palladium catalyst to give coupled products (**1**) and (**2**) (Scheme 1).[5] The path of this reaction may

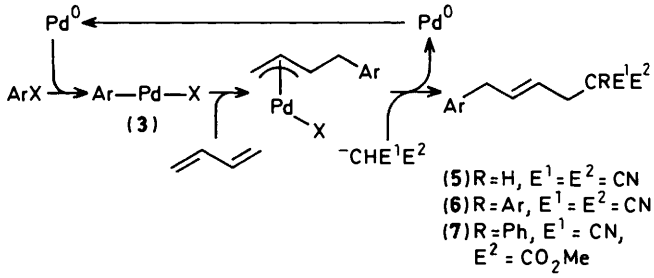


Scheme 1.



Scheme 2.

be reasonably explained by postulating the initial formation of an arylpalladium intermediate (**3**) (Scheme 2), which may be able to undergo insertion of dienes to afford π-allylpalladium species. From this viewpoint, we expected that in the presence of



Scheme 3.

1,3-dienes the reaction of halogenoarenes with the stabilised anion would lead to a new type of reaction in which three components are coupled together (Scheme 3). Here, we report that a palladium–phosphine complex catalyses the 1,4-arylation/alkylation reaction of buta-1,3-diene with halogenoarenes and stabilised anions such as $^-CH(CN)_2$, $^-CH(CN)O_2Me$, and $^-CH(CO_2Et)_2$, where two carbon–carbon bonds are built up from three components by a tandem insertion/coupling reaction in one catalytic cycle. Catalytic 1,4-arylation/alkylation reactions of 1,3-dienes have not appeared so far in literatures,[6] though a number of carbonylative coupling reactions[7] and several examples of catalytic tandem insertion/coupling reactions, *e.g.* 1,2-diene,[8] 1,3-diene,[9] norbornene,[10] methylenecyclopropane,[11] or isocyanide,[12] have been reported.

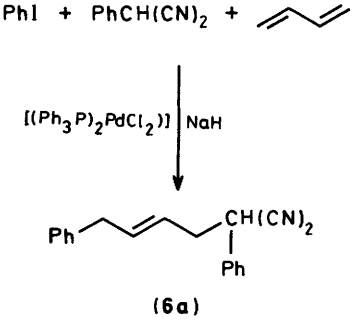
Results and Discussion

1,4-Arylation/Alkylation of Buta-1,3-diene with Malononitrile.—In our first attempt, we carried out the coupling reaction of halogenoarenes with malononitrile in the presence of an excess of buta-1,3-diene, *i.e.* a mixture of 10 mmol of iodobenzene and malononitrile anion, generated *in situ* from 11 mmol of malononitrile and NaH, was allowed to react with a large excess of buta-1,3-diene in the presence of dichlorobis(triphenylphosphine)palladium, $[PdCl_2(PPh_3)_2]$, catalyst. The product obtained from the reaction showed $m/z = 272$ in the mass spectrum which corresponds to the molecular formula of $C_{19}H_{16}N_2$, not to $C_{13}H_{12}N_2$ (**5**) ($m/z = 196$) (see Scheme 3). In the ^1H NMR spectrum, two kinds of olefinic protons were observed at δ 5.51 (1 H) and 5.88 (1 H) ppm as doublets of triplets along with aromatic protons (7.1–7.6 ppm; multiplet, 10 H). Two signals attributable to methylene groups appeared at 2.92 (2 H) and 3.41 (2 H) ppm as doublets. However, no methine proton attributable to a dicyanomethyl group was observed (see Experimental section). In the IR spectrum an absorption due to ν_{CN} appeared at 2 240 cm^{-1}. These spectral data indicate the product to be *trans*-5,5-dicyano-1,5-diphenylpent-2-ene (**6a**)

Table 1. 1,4-Arylation/alkylation of buta-1,3-diene with malononitrile.

	ArX	Temp. (°C)	Time (h)	Product		Yield[a] (%)
1	PhI	70	67	$PhCH_2CH{=}CHCH_2C(CN)_2$ (Ph)	(6a)	62
2	PhBr	70	48	$PhCH_2CH{=}CHCH_2C(CN)_2$ (Ph)	(6a)	10[b]
3	*p*-MeC_6H_4I	70	48	*p*-$MeC_6H_4CH_2CH{=}CHCH_2C(CN)_2$ (C_6H_4Me-*p*)	(6b)	46
4	*m*-MeC_6H_4I	70	48	*m*-$MeC_6H_4CH_2CH{=}CHCH_2C(CN)_2$ (C_6H_4Me-*m*)	(6c)	40
5	*o*-MeC_6H_4I	70	67	*o*-$MeC_6H_4CH_2CH{=}CHCH_2C(CN)_2$ (C_6H_4Me-*o*)	(6d)	0
				o-$MeC_6H_4CH(CN)_2$	(1a)	74
6	*p*-ClC_6H_4I	80	120	*p*-$ClC_6H_4CH_2CH{=}CHCH_2C(CN)_2$ (C_6H_4Cl-*p*)	(6e)	36
7	PhI	70	48	$PhCH_2CH{=}CHCH_2C(CN)CO_2Me$ (Ph)	(7)	42

[a] Isolated yield based on malononitrile or methyl cyanoacetate used. [b] Yield was determined by GLC based on malononitrile used.



(6a)

Scheme 4.

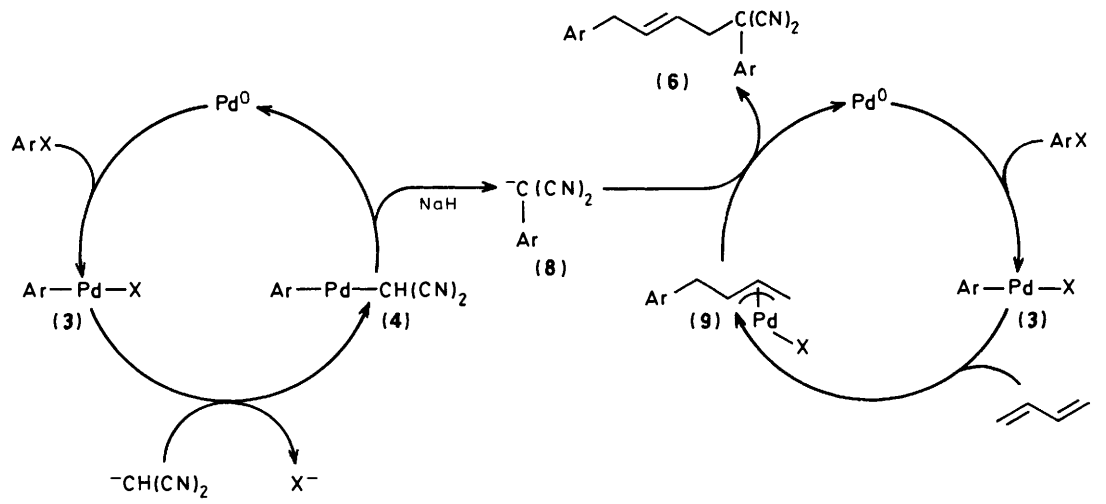
which may be derived from 2 mol equiv. of iodobenzene, 1 mol equiv. of malononitrile, and 1 mol equiv. of buta-1,3-diene (see Scheme 3). This is a rather unexpected result because of the use of equimolar proportions of malononitrile and iodobenzene. The formation of (**6a**) implied that the coupling reaction of iodobenzene with a malononitrile anion preceded nucleophilic attack of the anion on a π-allylic palladium species.

Thus, we carried out the reaction using an excess of halogenoarenes in order to obtain compound (**6**) in a good yield; thus in the presence of the palladium catalyst, 30 mmol of halogenoarenes were allowed to react with malononitrile anion, generated *in situ* from malononitrile (10 mmol) NaH (30 mmol), and a large excess of buta-1,3-diene. The results obtained here are summarized in Table 1. Iodobenzene gave the 1,4-arylation/alkylation product (**6a**) in 62% yield along with a small amount of biphenyl. *p*- and *m*-Iodotoluene similarly reacted to give the corresponding products. However *o*-iodotoluene gave the simple coupled product *o*-tolylmalononitrile (**1a**) in 74% yield and no 1,4-arylation/alkylation product (**6d**). The steric effect due to the *ortho*-methyl group in the *o*-tolylmalononitrile anion may limit attack of the anion on a π-allylpalladium species. *p*-Chloroiodobenzene required a higher temperature and longer reaction time. The reactivity of halogenoarenes was in the same order as observed previously in the cyanomethylation of halogenoarenes, I > Br ≫ Cl. Bromobenzene reacted with malononitrile and buta-1,3-diene to give the corresponding product (**6a**) in a low yield.

Previously we have reported that alkyl cyanoacetates also react with halogenoarenes to yield alkyl arylcyanoacetates.[5b] Hence, it seemed likely that 1,4-arylation/alkylation of butadiene proceeds with methyl cyanoacetate as a nucleophile instead of malononitrile (Table 1, run 7). In fact, we have confirmed that methyl cyanoacetate also reacts with iodobenzene and butadiene, giving the 1,4-arylation/alkylation product (**7**) in 42% yield.

On the other hand, under the same conditions the use of phenylmalononitrile as a nucleophile instead of malononitrile afforded (**6a**) in 70% yield (Scheme 4), indicating that the insertion of butadiene into the Pd–Ar bond proceeds after the dicyanomethylation of halogenoarenes. On the basis of the experimental results, we propose overall the reaction path shown in Scheme 5 in which two catalytic cycles [cycles (a) and (b)] operate in the arylation/alkylation system. In the initial step, arylmalononitriles are produced from the coupling reaction between halogenoarenes and malononitrile [cycle (a)], and the insertion reaction of buta-1,3-diene into the Pd–Ar bond [cycle (b)] must take place more slowly than the coupling reaction. The attack of the anion (**8**), which is generated from arylmalononitrile and the excess base, on the intermediate (**9**) then yields the 1,4-arylation/alkylation products (**6**) [cycle (b)]. As described above, *o*-iodotoluene gave no 1,4-arylation/alkylation product, but simply coupled product (**1a**). In this case cycle (a) smoothly proceeded to give (**1a**), the anion of (**1a**) being too sterically large to attack the π-allylpalladium intermediate (**9**), cycle (b) thus being stopped and no 1,4-arylation/alkylation product being formed. It is known that reactions of π-allylpalladium complexes with stabilized anions smoothly occur under mild conditions,[3] however, the present reaction requires somewhat forcing reaction conditions. This may be due to the relatively stable Pd–Ar bond, into which the insertion of butadiene [(**3**) to (**9**)] seems to need forcing conditions.

1,4-*Arylation/Alkylation with Diethyl Malonate.*—Under the conditions adopted in the cross-coupling reaction between iodobenzene and malononitrile (Scheme 1), the reaction of diethyl malonate with iodobenzene gave no cross-coupled product, diethyl phenylmalonate, biphenyl being obtained instead with recovery of diethyl malonate. However, it is well known that dialkyl malonates act as a good nucleophile and easily react with π-allylpalladium species to give allyl-substituted malonates.[3] Thus, we attempted to apply the present 1,4-arylation/alkylation reaction to diethyl malonate.



Scheme 5.

Table 2. 1,4-Arylation/alkylation of buta-1,3-diene with diethyl malonate.

	ArX	Temp. (°C)	Time (h)	Product		Yield[a] (%)
1	PhI	80	48	$PhCH_2CH{=}CHCH_2CH(CO_2Et)_2$	(10a)	51
				$(PhCH_2CH{=}CHCH_2)_2C(CO_2Et)_2$	(11a)	23
2	PhBr	80	48	$PhCH_2CH{=}CHCH_2CH(CO_2Et)_2$	(10a)	29[b]
				$(PhCH_2CH{=}CHCH_2)_2C(CO_2Et)_2$	(11a)	0
3	p-MeC_6H_4I	80	48	p-$MeC_6H_4CH_2CH{=}CHCH_2CH(CO_2Et)_2$	(10b)	54
				$(p$-$MeC_6H_4CH_2CH{=}CHCH_2)_2C(CO_2Et)_2$	(11b)	23
4	o-MeC_6H_4I	80	48	o-$MeC_6H_4CH_2CH{=}CHCH_2CH(CO_2Et)_2$	(10c)	35
				$(o$-$MeC_6H_4CH_2CH{=}CHCH_2)_2C(CO_2Et)_2$	(11c)	11
5	p-ClC_6H_4I	80	144	p-$ClC_6H_4CH_2CH{=}CHCH_2CH(CO_2Et)_2$	(10d)	46
				$(p$-$ClC_6H_4CH_2CH{=}CHCH_2)_2C(CO_2Et)_2$	(11d)	27

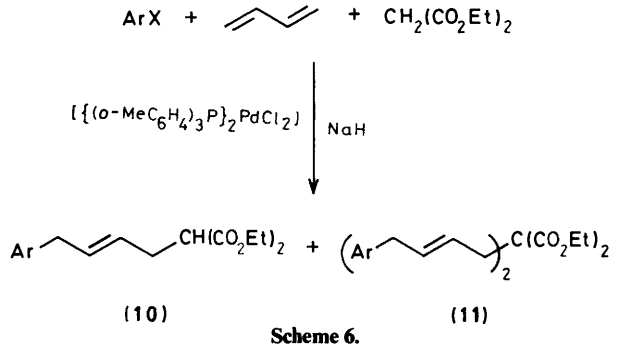
[a] Isolated yield based on charged halogenoarene. [b] Yield was determined by GLC based on charged bromobenzene.

Table 3. 1,4-Arylation/alkylation of buta-1,3-diene with diethyl alkylmalonate and iodobenzene.

$$PhI + C_4H_6 + RCH(CO_2Et)_2 \longrightarrow PhCH_2CH{=}CHCH_2\underset{\displaystyle Ph}{\underset{|}{C}}(CO_2Et)_2$$

	R	Temp. (°C)	Time (h)	Yield[a] (%)	
1	$PhCH_2$	80	48	84	(12a)
2	n-C_8H_{17}	80	48	50	(12b)

[a] Isolated yield based on charged iodobenzene.



Scheme 6.

In the presence, of dichlorobis(tris-*o*-tolylphosphine)palladium catalyst, an equimolar mixture of iodobenzene and diethyl malonate anion was allowed to react with a large excess of buta-1,3-diene. Two kinds of products were obtained (Scheme 6). The expected 1,4-arylation/alkylation product (**10a**) was obtained in 51% yield together with the further reaction product (**11a**) in 23% yield. Products (**10**) and (**11**) were identified on the basis of their mass, NMR and IR spectral results. Halogenoarenes such as *o*- and *p*-iodotoluene and *p*-chloroiodobenzene similarly yield the arylation/alkylation products (Table 2). Product (**11**) was derived from the further reaction of the monoalkylation product (**10**) with butadiene and halogenoarene, the latter still having an acidic proton capable of forming carbanion which can attack the π-allylpalladium species to give (**11**). Although the 1,4-arylation/alkylation of buta-1,3-diene with *o*-iodotoluene and malononitrile anion did not proceed because of steric factors associated with the *o*-tolylmalononitrile anion (Table 1, run 5), the reaction with *o*-iodotoluene and diethyl malonate gave the corresponding products (**10c**) and (**11c**) (Table 2, run 4). In the latter case, malonate and alkylmalonate (**10**) anions, which are sterically smaller than the *o*-tolylmalononitrile anion allow diethyl malonate to react smoothly with the π-allylic palladium intermediate to yield (**10c**) and (**11c**) in moderate yields. Similarly, alkyl-substituted diethyl malonate reacted with iodobenzene to yield the 1,4-arylation/alkylation product (**12**) of buta-1,3-diene (Table 3).

Experimental

B.p.s are uncorrected. IR spectra were recorded as thin films on a HITACH 295 Infrared Spectrophotometer. ^{1}H NMR spectra were measured in $CDCl_3$ with $SiMe_4$ as internal standard and recorded on a Bruker AM360 spectrometer. Upfield shifts are quoted as negative. EI mass spectra were taken with a JEOL JMS-06 spectrometer. Analytical vapour-phase chromatography was performed on a Shimazu GC-12A gas chromatograph equipped with a 3 m × 3 mm column (Silicon OV-11, 5% on Chromosorb W/AW 60–80 mesh).

General Procedure for the Reaction of Buta-1,3-diene with Halogenoarene and Malononitrile (or Methyl Cyanoacetate).—To a suspension of sodium hydride (60% in mineral oil; 1.20 g, 30 mmol) in THF (20 ml) at room temperature was added a solution of malononitrile (or methyl cyanoacetate) (10 mmol) in THF (10 ml) under a nitrogen atmosphere. After generation of the anion, a solution of halogenoarene (30 mmol) in THF (10 ml) and dichlorobis(triphenylphosphine)palladium (0.21 g, 0.3 mmol) were added to it; the mixture was then placed into a 100 ml stainless-steel autoclave. Buta-1,3-diene (*ca.* 10 ml, *ca.* 120 mmol) was introduced into the autoclave and allowed to react at 70–80 °C for *ca.* 2 days. After quenching of the reaction with dilute hydrochloric acid (1M; 30 ml), the product was extracted with diethyl ether (3 × 30 ml). The combined extracts were dried ($MgSO_4$) and evaporated to give a crude, brown viscous oil. This was purified by column chromatography on silica gel with hexane–dichloromethane (3:2) as eluant, followed by distillation to give the pure product (**6**).

trans-5,5-*Dicyano*-1,5-*diphenylpent*-2-*ene* (**6a**), a colourless oil (1.69 g, 62%), b.p. 115 °C at 0.05 mmHg (Found: C, 83.85; H, 5.95; N, 10.0. $C_{19}H_{16}N_2$ requires C, 83.79; H, 5.92; N, 10.28%); ν_{max}(neat) 2 240, 1 510, 1 505, 965, and 810 cm^{-1}; δ_H 2.92 (2 H, d, *J* 7 Hz), 3.41 (2 H, d, *J* 7 Hz), 5.51 (1 H, dt, 15, *J* 7 Hz), 5.88 (1 H, dt, *J* 15, 7 Hz), and 7.1–7.6 (10 H, m); *m/z* 272.

trans-5,5-*Dicyano*-1,5-*bis*(p-*tolyl*)*pent*-2-*ene* (**6b**), a colourless oil (1.38 g, 46%), b.p. 132 °C at 0.03 mmHg (Found: C, 83.75; H, 6.95; N, 9.4. $C_{21}H_{20}N_2$ requires C, 83.96; H, 6.71; N, 9.33%); ν_{max}(neat) 2 140, 965, and 805 cm^{-1}; δ_H 2.32 (3 H, s), 2.39 (3 H, s), 2.88 (2 H, d, *J* 7 Hz), 3.35 (2 H, d, *J* 7 Hz), 5.47 (1 H, dt, *J* 15, 7 Hz), 5.84 (1 H, dt, *J* 15, 7 Hz), 6.99 (2 H, d, *J* 8 Hz), 7.08 (2 H, d, *J* 8 Hz), 7.25 (2 H, d, *J* 8 Hz), and 7.39 (2 H, d, *J* 8 Hz); *m/z* 300.

trans-5,5-*Dicyano*-1,5-*bis*(m-*tolyl*)*pent*-2-*ene* (**6c**), a colourless oil (1.20 g, 40%), b.p. 113 °C at 0.04 mmHg (Found: C, 84.1; H, 6.4; N, 9.55. $C_{21}H_{20}N_2$ requires C, 83.96; H, 6.71; N, 9.33%); ν_{max}(neat) 2 240, 970, 780, and 695 cm^{-1}; δ_H 2.32 (3 H, s), 2.40 (3 H, s), 2.90 (2 H, d, *J* Hz), 3.37 (2 H, d, *J* 7 Hz), 5.50 (1 H, dt, *J* 15, 7 Hz), 5.89 (1 H, dt, *J* 15, 7 Hz), and 6.90–7.38 (8 H, m); *m/z* 300.

trans-5,5-*Dicyano*-1,5-*bis*(1-*chlorophenyl*)*pent*-2-*ene* (**6e**), a pale yellow oil (1.23 g, 36%), b.p. 186 °C at 0.05 mmHg (Found: C, 66.6; H, 4.3; Cl, 20.55; N, 8.45. $C_{19}H_{14}Cl_2N_2$ requires C, 66.88; H, 4.14; Cl, 20.78; N, 8.21%); ν_{max}(neat) 2 235, 965, and 810 cm^{-1}; δ_H 2.90 (2 H, d, *J* 7 Hz), 3.36 (2 H, d, *J* Hz), 5.46 (1 H, dt, *J* 15, 7 Hz), 5.82 (1 H, dt, *J* 15, 7 Hz), 7.01 (2 H, d, *J* 8 Hz), 7.24 (2 H, d, *J* 8 Hz), and 7.44 (4 H, s); *m/z* 341.

o-Tolylmalononitrile (**1a**), colourless needles (1.15 g, 74%), m.p. 49–50 °C (lit.,[13] 49–50 °C); ν_{max}(Nujol) 2 250 cm^{-1}; δ_H 2.48 (3 H, s), 5.04 (1 H, s), and 7.28–7.38 (4 H, m); *m/z* 156.

Ethyl 2-*cyano*-6-*phenylhex*-4-*enoate* (**7**), a colourless oil (1.28 g, 42%), b.p. 119 °C at 0.05 mmHg (Found C, 78.65; H, 6.35; N, 4.8. $C_{20}H_{19}NO_2$ requires C, 78.66; H, 6.27; N, 4.59%); ν_{max}(neat) 2 250, 1 765, 750, 730, and 700 cm^{-1}; δ_H 2.84 (1 H, dd, *J* 14, 8 Hz), 3.10 (1 H, dd, *J* 14, 8 Hz), 3.33 (2 H, d, *J* 8 Hz), 3.75 (3 H, s), 5.48 (1 H, dt, *J* 15, 8 Hz), 5.79 (1 H, dt, *J* 15, 8 Hz), and 7.06–7.55 (10 H, m); *m/z* 305.

Reaction of Buta-1,3-diene with Iodobenzene and Phenylmalononitrile.—To a suspension of sodium hydride (60% in mineral oil; 0.80 g, 20 mmol) in THF (20 ml) at room temperature was added a solution of phenylmalononitrile (1.42 g, 10 mmol) in THF (10 ml) under a nitrogen atmosphere. After generation of the anion, a solution of iodobenzene (3.06 g, 15 mmol) in THF (10 ml) and dichlorobis(triphenylphosphine)-palladium (0.21 g, 0.3 mmol) were added to it; the mixture was then placed into a 100 ml stainless-steel autoclave. Buta-1,3-diene (*ca.* 10 ml, *ca.* 120 mmol) was introduced into the autoclave and allowed to react at 70 °C for 48 h. After quenching of the reaction with dilute hydrochloric acid (1M; 30 ml), the product was extracted with diethyl ether (30 ml × 3). The combined extracts were dried ($MgSO_4$) and evaporated to give a crude, brown viscous oil; the yield (70%) of (**6a**) based on phenylmalononitrile was determined by gas chromatography.

General Procedure for the Reaction of Buta-1,3-diene with Halogenoarenes and Diethyl Malonate.—To a suspension of sodium hydride (60% in mineral oil; 0.44 g, 11 mmol) in THF (20 ml) at room temperature was added a solution of diethyl malonate (1.60 g, 10 mmol) in THF (10 ml) under a nitrogen atmosphere. After generation of the anion, a solution of halogenoarene (10 mmol) in THF (10 ml) and dichlorobis(tri-*o*-tolylphosphine)palladium (0.24 g, 0.3 mmol) were added to it; the mixture was then placed into a 100 ml stainless-steel autoclave. Buta-1,3-diene (*ca.* 10 ml, *ca.* 120 mmol) was introduced into the autoclave and allowed to react at 80 °C for 48 h. After quenching of the reaction with dilute hydrochloric acid (1M; 30 ml), the product was extracted with diethyl ether (30 ml × 3). The combined extracts were dried ($MgSO_4$) and evaporated to give a crude, brown viscous oil. This was purified by column chromatography on silica gel with hexane–dichloromethane (3:2) as eluant, followed by distillation to give the pure products (**10**) and (**11**).

Diethyl (4-*phenylbut*-2-*enyl*)*malonate* (**10a**), a colourless oil (1.47 g, 51%), b.p. 125 °C at 0.06 mmHg (Found: C, 69.85; H, 7.2. $C_{17}H_{22}O_4$ requires C, 70.32; H, 7.64%); ν_{max}.(neat) 1 740, 965, 745, and 695 cm^{-1}; δ_H 1.23 (6 H, t, *J* 7 Hz), 2.62 (2 H, dd, *J* 8, 7 Hz), 3.10 (2 H, d, *J* 7 Hz), 3.39 (1 H, t, *J* 8 Hz), 4.16 (4 H, q, *J* 7 Hz), 5.48 (1 H, dt, *J* 15, 7 Hz), 5.69 (1 H, dt, *J* 15, 7 Hz), and 7.12–7.31 (5 H, m); *m/z* 289.

Diethyl bis(4-*phenylbut*-2-*enyl*)*malonate* (**11a**), a colourless oil (0.48 g, 23%), b.p. 171 °C at 0.05 mmHg (Found: C, 77.1; H, 7.65. $C_{27}H_{32}O_4$ requires C, 77.11; H, 7.67%); ν_{max}(neat) 1 740, 965, 745, and 695 cm^{-1}; δ_H 1.17 (6 H, t, *J* 7 Hz), 2.62 (4 H, d, *J* 7 Hz), 3.29 (4 H, d, *J* 7 Hz), 4.10 (4 H, q, *J* 7 Hz), 5.36 (2 H, dt, *J* 15, 7 Hz), 5.61 (2 H, dt, *J* 15, 7 Hz), and 7.10–7.30 (10 H, m); *m/z* 420.

Diethyl [4-(p-*tolyl*)*but*-2-*enyl*]*malonate* (**10b**), a colourless oil (1.64 g, 54%), b.p. 121 °C at 0.07 mmHg (Found: C, 71.15; H, 7.81. $C_{18}H_{24}O_4$ requires C, 71.03; H, 7.95%); ν_{max}(neat) 1 745, 970, and 805 cm^{-1}; δ_H 1.23 (6 H, t, *J* 8 Hz), 2.30 (3 H, s), 2.61 (2 H, dd, *J* 8, 7 Hz), 3.26 (2 H, d, *J* 7 Hz), 3.39 (1 H, t, *J* 8 Hz), 4.16 (4 H, q, *J* 8 Hz), 5.46 (1 H, dt, *J* 15, 7 Hz), 5.67 (1 H, dt, *J* 15, 7 Hz), 7.02 (2 H, d, *J* 8 Hz), and 7.08 (2 H, d, *J* 8 Hz); *m/z* 304.

Diethyl bis[4-(p-*tolyl*)*but*-2-*enyl*]*malonate* (**11b**), a colourless oil (1.04 g, 23%), b.p. 176 °C at 0.06 mmHg (Found: C, 77.65; H, 8.0. $C_{29}H_{36}O_4$ requires C, 77.65; H, 8.09%); ν_{max}(neat) 1 740, 965, and 805 cm^{-1}; δ_H 1.19 (6 H, t, *J* 8 Hz), 2.30 (6 H, s), 2.60 (4 H, d, *J* 7 Hz), 3.25 (4 H, d, *J* 7 Hz), 4.11 (4 H, q, *J* 8 Hz), 5.34 (2 H, dt, *J* 15, 7 Hz), 5.59 (2 H, dt, *J* 15, 7 Hz), 7.01 (4 H, d, *J* 8 Hz), and 7.07 (4 H, d, *J* 8 Hz); *m/z* 448.

Diethyl [4-(o-*tolyl*)*but*-2-*enyl*]*malonate* (**10c**), a colourless oil (1.06 g, 35%), b.p. 117 °C at 0.05 mmHg (Found: C, 71.2; H, 7.8. $C_{18}H_{24}O_4$ requires C, 71.03; H, 7.95%); ν_{max}(neat) 1 740, 965, and 745 cm^{-1}; δ_H 1.23 (6 H, t, *J* 7 Hz), 2.25 (3 H, s), 2.61 (2 H, dd, *J* 8, 7 Hz), 3.29 (2 H, d, *J* 7 Hz), 3.37 (1 H, t, *J* 8 Hz), 4.18 (4 H, q, *J* 7 Hz), 5.38 (1 H, dt, *J* 14, 7 Hz), 5.66 (1 H, dt, *J* 14, 7 Hz), and 7.08–7.15 (4 H, m); *m/z* 304.

Diethyl bis[4-(o-*tolyl*)*but*-2-*enyl*]*malonate* (**11c**), a colourless

oil (0.24 g, 11%), b.p. 173 °C at 0.06 mmHg (Found: C, 77.75; H, 7.85. $C_{29}H_{36}O_4$ requires C, 77.65; H, 8.09%); ν_{max}(neat) 1 745, 965, and 745 cm^{-1}; δ_H 1.15 (6 H, t, *J* 7 Hz), 2.22 (6 H, s), 2.59 (4 H, d, *J* 7 Hz), 3.28 (4 H, d, *J* 7 Hz), 4.07 (4 H, q, *J* 8 Hz), 5.11 (2 H, dt, *J* 15, 7 Hz), 5.64 (2 H, dt, *J* 15, 7 Hz), and 7.07–7.37 (8 H, m); *m/z* 448.

Diethyl [4-(p-*chlorophenyl*)*but*-1-*enyl*]*malonate* (**10d**), a pale yellow oil (1.48 g, 46%), b.p. 140 °C at 0.07 mmHg (Found: C, 63.0; H, 6.5; Cl, 11.15. $C_{17}H_{21}ClO_4$ requires C, 62.86; H, 6.52; Cl, 10.92%); ν_{max}(neat) 1 750, 970, and 805 cm^{-1}; δ_H 1.24 (6 H, t, *J* 7 Hz), 2.62 (2 H, dd, *J* 8, 7 Hz), 3.27 (2 H, d, *J* 7 Hz), 3.40 (1 H, t, 8 Hz), 4.17 (4 H, q, *J* 7 Hz), 5.47 (1 H, dt, *J* 15, 7 Hz), 5.65 (1 H, dt, *J* 15, 7 Hz), 7.06 (2 H, d, *J* 8 Hz), and 7.23 (2 H, d, *J* 8 Hz); *m/z* 324.

Diethyl bis[4-(p-*chlorophenyl*)*but*-2-*enyl*]*malonate* (**11d**), a pale yellow oil (0.66 g, 27%), b.p. 165 °C at 0.06 mmHg (Found: C, 65.75; H, 5.7; Cl, 14.15. $C_{27}H_{30}Cl_2O_4$ requires C, 66.26; H, 6.18; Cl, 14.49%); ν_{max}(neat) 1 740, 965, and 805 cm^{-1}; δ_H 1.20 (6 H, t, *J* 7 Hz), 2.60 (4 H, d, *J* 7 Hz), 3.26 (4 H, d, *J* 7 Hz), 4.13 (4 H, q, *J* 7 Hz), 5.33 (2 H, dt, *J* 15, 7 Hz), 5.50 (2 H, dt, *J* 15, Hz), 7.04 (4 H, d, *J* 8 Hz), and 7.23 (4 H, d, *J* 8 Hz); *m/z* 488.

Reaction of Buta-1,3-diene with Iodobenzene and Alkyl-substituted Diethyl Malonate.—To a suspension of sodium hydride (60% in mineral oil; 0.44 g, 11 mmol) in THF (20 ml) at room temperature was added a solution of diethyl alkylmalonate (10 mmol) in THF (10 ml) under a nitrogen atmosphere. After generation of the anion, a solution of iodobenzene (2.04 g, 10 mmol) in THF (10 ml) and dichlorobis(tri-*o*-tolylphosphine)-palladium (0.24 g, 0.3 mmol) were added to it; the mixture was then placed into a 100 ml stainless-steel autoclave. Buta-1,3-diene (*ca.* 10 ml, *ca.* 120 mmol) was introduced into the autoclave and allowed to react at 80 °C for 48 h. After quenching of the reaction with dilute hydrochloric acid (1M; 30 ml), the product was extracted with diethyl ether (30 ml × 3). The extract was dried ($MgSO_4$) and evaporated to give a crude, brown viscous oil, which was purified by column chromatography on silica gel with hexane–dichloromethane (3:2) as eluant, followed by distillation to give the pure product (**12**).

Diethyl benzyl(4-*phenylbut*-2-*enyl*)*malonate* (**12a**), a colourless oil (3.19 g, 84%), b.p. 151 °C at 0.05 mmHg (Found: C, 75.7; H, 7.2. $C_{24}H_{28}O_4$ requires C, 75.76; H, 7.42%); ν_{max}(neat) 1 740, 965, 740, and 695 cm^{-1}; δ_H 1.19 (6 H, t, *J* 7 Hz), 2.54 (2 H, d, *J* 7 Hz), 3.24 (2 H, s), 3.36 (2 H, d, *J* 7 Hz), 4.14 (4 H, q, *J* 7 Hz), 5.49 (1 H, dt, *J* 15, 7 Hz), 5.68 (1 H, dt, *J* 15, 7 Hz), and 6.97–7.23 (10 H, m); *m/z* 380.

Diethyl octyl(4-*phenylbut*-2-*enyl*)*malonate* (**12b**), a colourless oil (2.01 g, 50%), b.p. 137 °C at 0.05 mmHg (Found: C, 74.3; H, 9.3. $C_{25}H_{38}O_4$ requires C, 74.59; H, 9.51%); ν_{max}(neat) 1 740, 965, 735, and 695 cm^{-1}; δ_H 0.88 (3 H, t, *J* 7 Hz), 1.24 (12 H, br), 1.89 (2 H, br), 2.62 (2 H, d, 7 Hz), 3.31 (2 H, d, *J* 7 Hz), 4.16 (4 H, q, *J* 8 Hz), 5.37 (1 H, dt, *J* 15, 7 Hz), 5.64 (1 H, dt, *J* 15, 7 Hz), and 7.13–7.20 (5 H, m); *m/z* 380.

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