Palladium-catalysed Allylic Alkylation of Allylic Nitro Compounds with Stabilized Carbanions
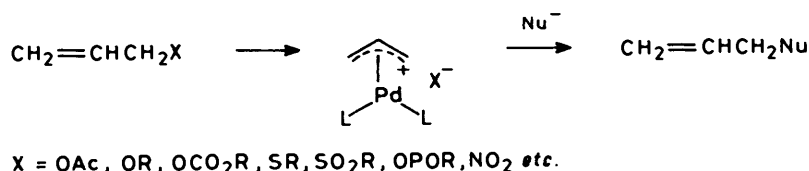
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In the presence of a catalytic amount of $Pd(PPh_3)_4$, allylic nitro compounds (1) undergo allylic alkylation with stabilized carbanions to give a mixture of two regio-isomers (2) and (3). The product ratio (2) : (3) is controlled both by the nature of the substituents of π-allyl unit and the steric factors of the nucleophiles and ligands.

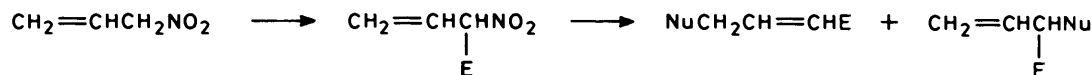Palladium-catalysed allylic alkylations (Scheme 1) are extremely useful reactions; allyl acetates (X = OAc) being amongst the most commonly used substrates.[1]† the isomerization of a nitro alkene.[6] Compounds (1a, b, e, and g) were prepared by the former method and other compounds were prepared by the isomerization of 2-nitrobut-2-ene.[6]

$$CH_2=CHCH_2X \longrightarrow \quad \longrightarrow^{Nu^-} \quad CH_2=CHCH_2Nu$$

X = OAc, OR, OCO$_2$R, SR, SO$_2$R, OPOR, NO$_2$ *etc.*

Scheme 1.

In a previous communication, we reported that allylic nitro compounds (1; X = NO$_2$) undergo reaction with sodium dimethyl malonate similar to that depicted in Scheme 1.[2] Allylic nitro compounds are now being used as useful electrophiles in a number of reactions.[3] Thus, nucleophiles and electrophiles can be introduced stepwise as shown in Scheme 2. Although

Treatment of compound (1) with the sodium salt of dimethyl malonate in the presence of $Pd(PPh_3)_4$ (5 mol %) at reflux in tetrahydrofuran (THF) led to a smooth alkylation to give the substitution products (2) and (3). The results are summarized in Table 1. When R = Me, substitution occurred preferentially at the more substituted end and the ratio of

$$CH_2=CHCH_2NO_2 \longrightarrow CH_2=CHCHNO_2 \longrightarrow NuCH_2CH=CHE + CH_2=CHCHNu$$
$$\qquad\qquad\qquad\qquad\qquad\qquad |\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad E\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad E$$

Scheme 2.

electrophiles (E) can be introduced regioselectively at the α-position of the nitro group, it is not easy to control the regiochemistry of the second step in Scheme 2. Nucleophiles (Nu) can attack either the α- or the γ-carbon depending on the substituents present on the allylic components. The regiochemistry of the palladium-catalysed allylic alkylation of allylic acetates or related electrophiles has been well studied,[4] but as yet it is far from fully understood.[5]‡ In this paper we wish to report on the regiochemistry of palladium-catalysed allylation of compound (1), which may provide some clues to the understanding of the regiochemistry of this reaction.

Results and Discussion

A series of allylic nitro compounds (1) was prepared by either the introduction of a vinyl group onto the nitro compound or

(2):(3) was 73:27. This ratio decreased with increased bulkiness of the alkyl groups. When R was an electron-withdrawing group such as CO$_2$Et or CH$_2$OAc, the reaction gave compound (3) as the sole product with a predominance of the E-isomer. In this case, formation of (3) is favoured in both sterically and electronically. These phenomena can be explained in the same way as for the palladium-catalysed alkylation of allylic acetates.[4,7] The palladium atom is probably unsymmetrically positioned in the transition state with respect to the two ends of the allylic system, depending on the substitution. When R is an electron-donating group, the palladium atom lies closer to the γ-carbon (structure A), and when R is an electron-withdrawing group, the palladium atom lies closer to the α-carbon (structure B). If steric factors of the R groups and the nucleophiles are negligible, external nucleophiles should attack the α-carbon and the γ-carbon in the intermediate A and B, respectively. If steric factors are important, the nucleophiles should preferentially attack the least hindered site of the π-allyl system. Thus, the ratio of (2):(3) is controlled by these competing effects. The bulkier the nucleophile, the greater the importance of the steric factors. The reaction of compound (1a) with various nucleophiles was carried out and the results are summarized in Table 2. The ratio of (4):(5) [or (2a):(3a)] was affected by the bulkiness of the

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* Many kinds allylic substrate undergo the reaction of Scheme 1, for example, X = OAc,[1b] X = OCO$_2$R,[1c] X = SO$_2$R,[1d] and X = OP(O)R[1e]

‡ In general palladium-catalysed alkylation leads to substitution at the least hindered terminus, whilst other metal-catalysed reactions lead to substitution at the most hindered site. Thus the regiocontrol in these metal-assisted alkylations is still confusing.[5]
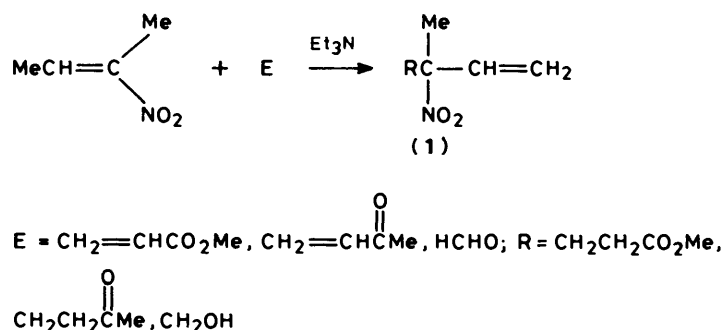
Scheme 3.
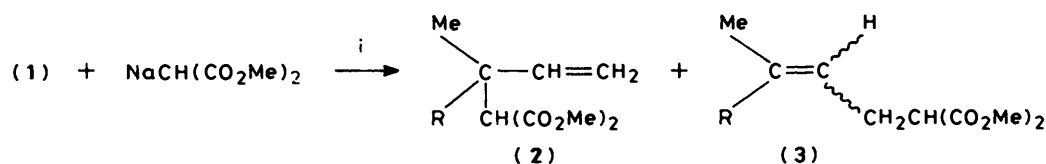
Scheme 4. *Reagents:* (i), Pd(PPh₃)₄ (5 mol %)-PPh₃ (20 mol%)-THF, 66°C
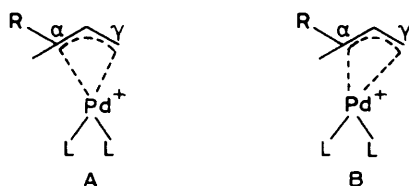
Table 1. Alkylation of compound (1) with dimethyl sodiomalonate[a]

(R)	Compd.	Time (h)	Product	Yield (%)	(2):(3)[b]	E:Z of (3)[b]
Me	(1a)	4	(2a) + (3a)	60	73:27	
n-C₆H₁₃	(1b)	6	(2b) + (3b)	78	42:58	71:29
CH₂CH₂CO₂Me	(1c)	6	(2c) + (3c)	66	36:64	75:25
CH₂CH₂COMe	(1d)	6	(2d) + (3d)	60	38:62	83:17
CH₂Ph	(1e)	8	(2e) + (3e)	77	18:82	82:18
CH₂OAc	(1f)	3	(3f)	91	0:100	85:15
CO₂Et	(1g)	9	(3g)	75	0:100	91:9
H	(1h)	9	(2h) + (3h)	36	54:46	

[a] The reaction was carried out by refluxing a mixture of compound (1), the nucleophile, Pd(PPh₃)₄ (5 mol%), and PPh₃ (20 mol%) in THF. [b] The ratios (2):(3) and E:Z were determined by g.l.c.; compound (2), (Z)-(3), and (E)-(3) appeared in this order on g.l.c. Their structures were determined by n.m.r. spectroscopy and g.c.—m.s. (see the Experimental section).

Table 2. Allylation of compound (1a) with various nucleophiles[a]

Nu	Time (h)	Product	Yield (%)	(4):(5) [(2a):(3a)]
NaCH(CN)CO₂Me	6	(4a)	75	99:1
NaCH(CO₂Me)₂	15	(2a) + (3a)	60	73:27
NaC(Me)(CO₂Et)₂	15	(4b) + (5b)	65	37:63
NaC(Me)SO₂C₆H₄Me-p | CO₂Et	15	(5c)	90	0:100

[a] The reaction was carried out under the same conditions as those given in Table 1.

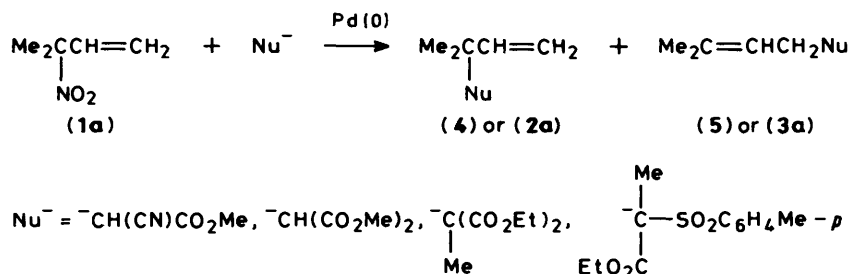**Table 3.** Effects of solvent, ligands, temperature, and time upon the regiochemistry

Entry	Compd.	Solvent	Reagent	Temp. (°C)	Time (h)	(2):(3)
1	(1a)	THF	None	66	15	80:20
2	(1a)	THF	PPh₃ (10 mol%)	66	5	73:27
3	(1a)	THF	PPh₃ (10 mol%)	66	15	75:25
4	(1a)	THF	DPPE (10 mol%)	66	15	60:40
5	(1a)	THF	DPPE (20 mol%)	66	15	34:64
6	(1a)	THF–HMPA	PPh₃ (20 mol%)	66	15	76:24
7	(1a)	MeCN	PPh₃ (20 mol%)	66	15	77:23
8	(1a)	DMF	PPh₃ (20 mol%)	66	15	75:25
9	(1a)	DMF	PPh₃ (20 mol%)	20	15	73:27
10	(1e)	THF	PPh₃ (10 mol%)	40	15	21:79
11	(1e)	THF	DPPE (10 mol%)	40	15	6:94
12	(1c)	THF	PPh₃ (20 mol%)	66	6	36:64
13	(1c)	THF	DPPE (10 mol%)	66	6	11:89
14	(1c)	THF	DPPE (20 mol%)	66	6	9:91
15	(1d)	THF	PPh₃ (10 mol%)	66	6	38:62
16	(1d)	THF	DPPE (10 mol%)	66	6	0:100

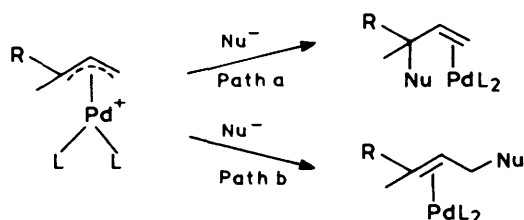The reaction was carried out in the same way as those described in Table 1.

nucleophiles. The regiochemistry of the reaction involving the sodium salt of methyl cyanoacetate was completely different from that using a nucleophile substituted with the sulphone moiety. The former nucleophile is sterically too small to attack the tertiary carbon, and the latter one is sterically too large to attack the primary carbon selectively.

The reaction of compound (1) with dimethyl sodiomalonate was carried out under various conditions to study the effect of time, temperature, solvents, and ligands on the regiochemistry of the reaction. The results are summarized in Table 3. Variation of time (entry 2 and 3), temperature (entry 8 and 9), and the solvent (entry 2, 6, 7, and 8) did not cause the change of the product ratio. However, the addition of DPPE* to the reaction
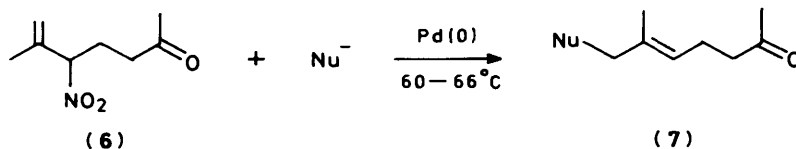
* DPPE = 1,2-Bis(diphenylphosphino)ethane

$$Me_2\overset{|}{\underset{NO_2}{C}}CH=CH_2 \ + \ Nu^- \ \xrightarrow{Pd(0)} \ Me_2\overset{|}{\underset{Nu}{C}}CH=CH_2 \ + \ Me_2C=CHCH_2Nu$$

(1a)　　　　　　　　　　　　　　　　　(4) or (2a)　　　　　　(5) or (3a)

$$Nu^- = {}^-CH(CN)CO_2Me, \ {}^-CH(CO_2Me)_2, \ {}^-\underset{Me}{\overset{Me}{C}}(CO_2Et)_2, \ {}^-\underset{EtO_2C}{\overset{Me}{C}}-SO_2C_6H_4Me-p$$

Scheme 5.

Scheme 6.

(6)　　　　　　　　　　　　　　　　　　　　　　　(7)

Scheme 7.

unit, and the ligand, and since also allylic nitro compounds are prepared by various methods,[6] the present reaction expands the utility of the palladium-catalysed allylation. In fact, the products, (2), (3), and (7), are important intermediates for the synthesis of various terpenoids.

Experimental

I.r. spectra were measured on a Hitachi 215 spectrometer. [1]H N.m.r. spectra were obtained with a JEOL PS-100 and a JEOL JX-400 spectrometer. Mass spectra were recorded on a JEOL

Table 4. Allylic alkylation of compound (6) with stabilized carbanions

Nu	Solvent	Time (h)	Product	Yield (%)	E:Z[a]
NaCH(CN)CO$_2$Me	DMF	8	(7a)	50	81:19
NaCH(COMe)-CO$_2$Me	THF	14	(7b)	62	83:17
NaCH(CO$_2$Me)$_2$	THF	8	(7c)	79	89:11
NaC(Me)CO$_2$Et	DMF	18	(7d)	85	93:7
$\overset{|}{S}O_2C_6H_4Me$—f					

[a] The E:Z ratio was determined by g.l.c., h.p.l.c. and n.m.r.

mixture caused the remarkable change of the ratio of (2):(3). This is usual for palladium-catalysed allylation.[4] The nucleophile attacks the π-allyl–palladium complex to form an alkene–palladium complex as shown in Scheme 6. When the ligands are smaller, path b is favoured, and this tendency is enhanced when nucleophiles and R are sterically hindered.

The reaction of (1h) with dimethyl sodiomalonate gave a 1:1 mixture of the products (2h) and (3h) (Table 1). Thus, it is rather difficult to control the regiochemistry between the primary and secondary carbon centres in such a simple case. However, the reaction of 6-methyl-5-nitro-hept-6-en-2-one (6) with stabilized carbanions gave a sole product (7). E-Trisubstituted alkenes were formed with ca. 80—90% stereoselectivity. E- and Z-Isomers were readily analysed by g.l.c., h.p.l.c., and n.m.r. spectroscopy, by which the actual configuration of these alkenes was determined. The vinyl methyl protons of these compounds resonated at δ 1.4—1.7 and those of E-isomers resonated at higher field than those of Z-isomers.[8] The results are summarized in Table 4. Thus, the nucleophilic attack occurred at the primary carbon regardless of the steric bulk of the nucleophiles.

As the regiochemistry of the second step can be well controlled by varying the nucleophile, substituents of the allyl

JMS-DX-300 spectrometer. G.l.c. analyses were performed with a Shimadzu GC-8A with a 2 m column packed with silicon DC-550. H.p.l.c. analyses were performed with a Hitachi 633-A chromatograph with ODS column and methanol–water (4:1) as the eluant. Elemental analyses were performed by the Kyoto University Microanalytical Laboratories. Allylic nitro compounds were prepared according to literature methods.[2,3,6]

Reaction of Compound (1) *with Dimethyl Sodiomalonate: General Procedure.*—To a stirred mixture of compound (1) (10 mmol), Pd(PPh$_3$)$_4$ (0.5 mmol), and PPh$_3$ (2 mmol) in THF (10 ml), was added a solution of the sodium salt of dimethyl malonate (20 mmol) in THF (30 ml). The resulting mixture was heated at about 60 °C for 8—15 h, and then poured into water, and extracted with diethyl ether. The organic layer was washed with brine and dried (MgSO$_4$). After filtration, the solvent was removed and the residue was purified by column chromatography (silica gel–benzene) to give compounds (2) and (3). The ratios product and E:Z were determined by g.l.c. and the structures were determined by n.m.r. spectroscopy and g.c.—m.s.

The following compounds were prepared; compounds (2) and (3) were separated by g.l.c.

Compound (2a): $v_{max.}$(neat) 1 730 cm^{-1}; δ(CDCl$_3$) 1.23 (6 H, s, Me), 3.38 (1 H, s, CH), 3.68 (6 H, s, OMe), 5.00 (1 H, d, J 11 Hz, CH=), 5.05 (1 H, d, J 17 Hz, CH=), and 6.00 (1 H, dd, J 11, 17 Hz, CH=).

Compound (3a): δ(CDCl$_3$) 1.64 (3 H, s, Me), 1.70 (3 H, s, Me), 2.59 (2 H, t, J 8 Hz, CH$_2$), 3.18 (1 H, t, J 8 Hz, CH), 3.68 (6 H, s, OMe), and 5.12 (1 H, t, J 8, CH=). These data are in good agreement with those reported.[9]

Compound (2b): $v_{max.}$(neat) 1 730 cm^{-1}; δ(CDCl$_3$) 0.90 (3 H, t, J 8 Hz, Me), 1.06—1.60 [10 H, m, (CH$_2$)$_5$], 1.22 (3 H, s, Me), 3.34 (1 H, s, CH), 3.67 (6 H, s, OMe), 4.90 (1 H, d, J 11 Hz, CH=), 5.00 (1 H, d, J 8 Hz, CH=), and 5.90 (1 H, dd, J 11, 18 Hz, CH=) (Found: M^+, 270.1831. C$_{15}$H$_{26}$O$_4$ requires M, 270.1819).

Compound (3b): (neat) 1 730 cm^{-1}; δ(CDCl$_3$) 0.92 (3 H, t, J 8

Hz, Me), 1.10—1.55 [8 H, m, $(CH_2)_4$], 1.62 (3 H, s, Me), 1.98 (2 H, m, CH_2), 2.60 (2 H, t, J 8 Hz, CH_2), 3.16 (1 H, t, J 8 Hz), 3.68 (6 H, s, OMe), and 5.10 (1 H, m, CH=) (Found: M^+, 270.1825).

Compound (**2c**): $v_{max.}$(neat) 1 730 cm^{-1}; δ(CDCl$_3$) 1.22 (3 H, s, Me), 2.12—2.40 (4 H, m, CH_2CH_2), 3.37 (1 H, s, CH), 3.60 (3 H, s, OMe), 3.68 (6 H, s, OMe), 4.98 (1 H, d, J 11 Hz, CH=), 5.05 (1 H, d, J 17 Hz, CH=), and 5.92 (1 H, dd, J 11, 17 Hz, CH=) (Found: M^+, 272.1166. $C_{13}H_{20}O_6$ requires M, 272.1259).

Compound (**3c**): $v_{max.}$(neat) 1 730 cm^{-1}; δ(CDCl$_3$) 1.63 (3 H, br s, Me), 2.2—2.4 (4 H, m, CH_2CH_2), 2.50 (2 H, t, J 8 Hz, CH_2), 3.34 (1 H, m, CH), 3.60 (3 H, s, OMe), 3.68 (6 H, s, OMe), and 5.12 (1 H, m, CH=) (Found: M^+, 272.1247).

Compound (**2d**): $v_{max.}$(neat) 1 700 and 1 730 cm^{-1}; δ(CDCl$_3$) 1.23 (3 H, s, Me), 2.13 (3 H, s, Me), 2.2—2.6 (4 H, m, CH_2CH_2), 3.35 (1 H, s, CH), 3.68 (6 H, s, OMe), 4.98 (1 H, d, J 11, Hz, CH=), 5.05 (1 H, d, J 17 Hz, CH=), and 5.92 (1 H, dd, J 11, 17 Hz) (Found: M^+, 256.1306. $C_{13}H_{20}O_5$ requires M, 256.1309).

Compound (**3d**): δ(CDCl$_3$) 1.63 (3 H, br s, Me), 2.14 (3 H, s, Me), 2.2—2.6 (6 H, m, CH_2CH_2), 3.40 (1 H, m, CH), 3.68 (6 H, s, OMe), 5.12 (1 H, m, CH=) (Found: M^+, 256.1309).

Compound (**2e**): $v_{max.}$(neat) 1 730 cm^{-1}; δ(CDCl$_3$) 1.21 (3 H, s, Me), 2.92 (2 H, s, CH_2), 3.40 (1 H, s, CH), 3.68 (6 H, s, OMe), 5.02 (1 H, d, J 11 Hz, CH=), 5.10 (1 H, d, J 17 Hz, CH=), 6.10 (1 H, dd, J 11, 17 Hz), and 7.2 (5 H, m, Ph) (Found: M^+ 276.1361. $C_{16}H_{20}O_4$ requires M, 276.1361).

Compound (**3e**): δ(CDCl$_3$) 1.66 (3 H, br s, Me), 2.65 (2 H, t, J 8 Hz, CH_2), 3.26 (2 H, s, CH_2), 3.44 (1 H, m, CH), 3.68 (6 H, s, OMe), 5.20 (1 H, m, CH=), and 7.2 (5 H, m, Ph); (Found: M^+, 276.1358).

Compound (E)-(**3f**): $v_{max.}$(neat) 1 720 cm^{-1}; δ(CDCl$_3$) 1.68 (3 H, s, Me), 2.04 (3 H, s, Me), 2.64 (2 H, t, J 8 Hz), 3.40 (1 H, t, J 8 Hz, CH), 3.68 (6 H, s, OMe), 4.40 (2 H, s, CH_2O), and 5.38 (1 H, m, CH=) (Found: M^+ − 59, 199.0977. $C_{10}H_{15}O_4$ requires M 59, 199.0971).

Compound (Z)-(**3f**): δ(CDCl$_3$) 1.70 (3 H, s, Me), 2.04 (3 H, s, Me), 2.64 (2 H, t, J 8 Hz, CH_2), 3.40 (1 H, t, J 8 Hz, CH), 3.68 (6 H, s, OMe), 4.58 (2 H, s, OCH_2), and 5.30 (1 H, m, CH=).

Compound (E)-(**3g**): $v_{max.}$(neat) 1 700 and 1 720 cm^{-1}; δ(CDCl$_3$) 1.28 (3 H, t, J 8 Hz, Me), 1.87 (3 H, s, Me), 2.76 (2 H, t, J 8 Hz, CH_2), 3.48 (1 H, t, J 8 Hz, CH), 3.70 (6 H, s, OMe), 4.16 (2 H, q, J 8 Hz, OCH_2), and 6.48 (1 H, m, CH=); (Found: M^+, 258.1089. $C_{12}H_{18}O_6$ requires M, 258.1102).

Compound (Z)-(**3g**): δ(CDCl$_3$) 3.00 (2 H, t, J 8 Hz, CH_2), 5.80 (1 H, m, CH=). Other peaks were the same as those described for compound (E)-(**3g**).

Compound (**3h**); See ref. 3.

Reaction of Compound (**1a**) *with Various Nucleophiles.*—The reaction was carried out according to the general procedures and following products were prepared by this reaction. The product ratio was determined by g.l.c. and n.m.r. spectroscopy.

Compound (**4a**): $v_{max.}$(neat) 1 730 and 2 210 cm^{-1}; δ(CDCl$_3$) 1.26 (6 H, s, Me), 3.41 (1 H, s, CH), 3.76 (3 H, s, OMe), 5.08 (1 H, d, J 11 Hz, CH=), 5.12 (1 H, d, J 17 Hz, CH=), and 5.82 (1 H, dd, J 11, 17 Hz, CH=) (Found: M^+, 167.1000. $C_9H_{13}NO_2$ requires M, 167.0995).

Compound (**4b**): $v_{max.}$(neat) 1 730 cm^{-1}; δ(CDCl$_3$) 1.20 (6 H, s, Me), 1.24 (3 H, s, Me), 1.30 (6 H, t, J 8 Hz, Me), 4.12 (4 H, q, J 8 Hz, OCH_2), 4.82 (1 H, d, J 11 Hz, CH=), 4.96 (1 H, d, J 17 Hz, CH=), and 6.02 (1 H, dd, J 11, 17 Hz, CH=) (Found: C, 64.15; H, 9.45. $C_{13}H_{22}O_4$ requires C, 64.43; H, 9.15%).

Compound (**5b**): δ(CDCl$_3$) 1.30 (6 H, t, J 8 Hz, Me), 1.38 (3 H, s, Me), 1.58 (3 H, s, Me), 1.64 (3 H, s, Me), 2.60 (2 H, d, J 8 Hz, CH_2), 4.16 (4 H, q, J 8 Hz, OCH_2), and 4.98 (1 H, m, CH=) (Found: C, 64.3; H, 9.35%).

Compound (**5c**): (neat) 1 150, 1 300, and 1 720 cm^{-1}; δ(CDCl$_3$) 1.20 (3 H, t, J 8 Hz, Me), 1.58 (3 H, s, Me), 1.60 (3 H, s, Me), 1.60 (3 H, s, Me), 1.68 (3 H, s, Me), 2.42 (3 H, s, Me), 2.6—3.1 (2 H, m,

CH_2), 4.16 (2 H, q, J 8 Hz, OCH_2), 4.96 (1 H, m, CH=), and 7.32 and 7.64 (4 H, ArH) (Found: C, 62.65; H, 7.45. $C_{17}H_{24}O_5S$ requires C, 62.93; H, 7.46%).

Reaction of Compound (**1**) *with the Sodium Salt of Dimethyl Malonate under Various Conditions.*—The reaction was carried out according to the general procedure. In some cases reagents other than triphenylphosphine were used; the reaction conditions are summarized in Table 3. The product ratio was determined by g.l.c. and n.m.r. spectroscopy.

Reaction of Compound (**6**) *with Methyl Cyanoacetate.*—To a stirred mixture of 6-methyl-5-nitrohept-6-en-2-one (**6**) (0.16 g, 0.94 mmol), Pd(PPh$_3$)$_4$ (100 mg), and triphenylphosphine (60 mg) in dimethylformamide (2 ml), was added a solution of the sodium salt of methyl cyanoacetate which was prepared *in situ* by the reaction of sodium hydride (50% dispersion; 0.063 g, 1.3 mmol) with methyl cyanoacetate (0.12 g, 1.2 mmol) in DMF (5 ml). The resulting mixture was heated at *ca.* 60 °C for 8 h, and then poured into water and extracted with diethyl ether. The organic layer was washed with brine and dried (MgSO$_4$). After filtration, the solvent was removed and the residue was purified by column chromatography (silica gel–benzene) to give compound (**7a**) (0.11 g, 50%), $v_{max.}$(neat) 1 700, 1 730, and 2 250 cm^{-1}; δ(CDCl$_3$) 1.72 (3 H, s, Me), 2.13 (3 H, s, Me), 2.15—2.64 (6 H, m, CH_2CH_2, CH_2), 3.76 (3 H, s, OMe), 3.70 (1 H, t, J 8 Hz, CH), and 5.29 (1 H, br t, CN=). The signal at δ 1.72 separated to two peaks when the spectrum was recorded at 400 MHz assigned to (E) (**7a**) at δ 1.713 and (Z)-(**7a**) at δ 1.730. The E:Z ratio was determined by integration of these two peaks (see Table 4). (Found: M^+, 223.1140. $C_{12}H_{17}NO_3$ requires M, 223.1161).

The following compounds were prepared by this procedure.

Compound (**7b**): $v_{max.}$(neat) 1 700, 1 720, and 1 740 cm^{-1}; δ(CDCl$_3$) 1.62 (3 H, s, Me), 2.12 (3 H, s, Me), 2.20 (3 H, s, Me), 2.2—2.6 (6 H, m, CH_2CH_2, CH_2), 3.60 (1 H, t, J 8 Hz, CH), 3.71 (3 H, s, OMe), and 5.08 (1 H, br t, CH=). The E/Z ratio was determined in the same way as for compound (**7a**); δ (400 MHz) 1.629 [(E)-(**7b**)] and 1.659 [(Z)-(**7b**)] (Found: M^+, 240.1311. $C_{13}H_{20}O_4$ requires M, 240.1361).

Compound (**7c**): $v_{max.}$(neat) 1 700 and 1 720 cm^{-1}; δ(CDCl$_3$) 1.61 (3 H, s, Me), 2.10 (3 H, s, Me), 2.16—2.58 (6 H, m, CH_2CH_2, CH_2), 3.46 (1 H, t, J 8 Hz), 3.68 (6 H, s, OMe), and 5.06 (1 H, br t, CH=). The E:Z ratio was determined by g.l.c. and n.m.r. spectroscopy δ (400 MHz) 1.615 (E-isomer) and 1.645 (Z-isomer). The structure was further confirmed by comparison with spectral data of the literature.[10]

Compound (**7d**): (E)- and (Z)-(**7d**) were separated by h.p.l.c. The E-isomer showed $v_{max.}$(neat) 1 150, 1 220, 1 300, 1 710, and 1 730 cm^{-1}; δ(CDCl$_3$) 1.21 (3 H, t, J 8 Hz, Me), 1.46 (3 H, s, Me), 1.48 (3 H, s, Me), 2.11 (3 H, s, Me), 2.2—2.6 (6 H, m, CH_2CH_2, CH_2), 2.45 (3 H, s, Me), 4.12 (2 H, q, J 8 Hz, OCH_2), 5.18 (1 H, br t, CH=), and 7.3 and 7.7 (4 H, ArH) (Found: C, 63.4; H, 7.4. $C_{20}H_{28}O_5S$ requires C, 63.13; H, 7.42%). The Z-isomer showed δ 1.22 (3 H, t, J 8 Hz), 1.48 (3 H, s, Me), 1.53 (3 H, s, Me), 2.16 (3 H, s, Me), 2.42 (3 H, s, Me), 2.2—2.8 (6 H, m, CH_2CH_2, CH_2), 4.16 (2 H, q, J 8 Hz), 5.22 (1 H, br t, CH=), and 7.3 and 7.4 (4 H, ArH). (Found: 63.35; H, 7.4%).

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