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ASYMMETRIC SYNTHESIS OF 4,4-DISUBSTITUTED ALKA-2,3-DIENOATES[1]†

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Abstract—The Horner–Emmons reaction of P-chiral carbanion 1 derived from the optically active 2 with a series of unsymmetrical ketenes leading to the title allene esters 4 is described. When (*S*)-(−)-2 was used as a starting material, the enantiomerically enriched (*R*)-(−)-**4a** as well as **4b** were obtained. On the basis of these results the stereochemical course of the Horner–Emmons reaction is discussed and configurations of the other allene esters obtained are proposed.

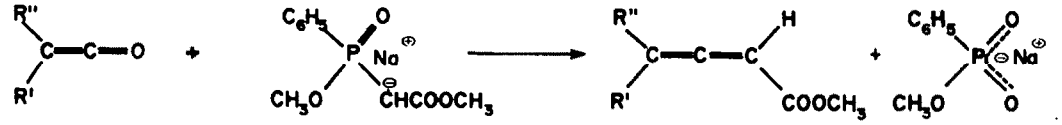
Among various methods for the synthesis of allene carboxylic esters, reactions involving phosphorus-containing starting materials as Wittig[2] or Horner–Emmons[3] reagents seem to be used more frequently. Particularly, the Horner–Emmons reagents made an important contribution to the progress in this area due to the milder reaction conditions required. However, from the Wittig reagents and either acid chlorides or ketenes, only α-substituted allene esters could be obtained because the α,β-acetylenecarboxylic esters were formed when ylids containing an α-hydrogen had been employed.[4,5] In order to obtain 4,4-disubstituted alka-2,3-dienoates only the Horner–Emmons reagents and ketenes have been successfully used.[2d,2e,3] Here, we would like to present our results on the asymmetric synthesis of such compounds from the optically active methyl O-methylphenylphosphinylacetate 2 and unsymmetrical ketenes as well as to discuss the stereochemical course of the Horner–Emmons reaction of phosphonate carbanion 1 with ketenes.

In preliminary studies racemic 2 was employed in the reaction under investigation (Scheme 1) in order to study the reactivities of the ketenes selected[6] (3) and to find the best method for the purification of esters 4 which would have been further followed with the optically active 2.

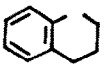
It was found that a short column chromatography on silicagel with the subsequent high vacuum distillation was the best method for purification of all allene esters except **4c**. The latter decomposed during distillation. Although esters **4a**, **4b**, **4e**, **4f** could be purified by distillation, they were not stable over long periods of time, eventually becoming yellow resins. Esters **4d**, **4g**, **4h** remained unchanged for 2 years. The yields of esters **4a–4d**, **4g**, **4h** (more than 40%) were considered satisfactory for the studies of the asymmetric synthesis and were not optimised. Numerous attempts at improving the yield of **4f** (4%) failed and for this reason the reaction of **3f** with optically active 2 was not studied.

The transformation of the allene esters 4 into the corresponding acids 5 was of interest because the absolute configuration and the optical purity of **5a** and **5b** were determined earlier.[5] From racemic **4a** and **4b** the corresponding acids **5a** and **5b** were prepared by alkaline hydrolysis. Again, **5c** was not obtained, probably due to polimerisation of **4c** and/or **5c** during reaction and work-up. On the other hand, **5e** was found to be unstable in the presence of acids and even at 0° slowly isomerised into 5-methyl-5-isopropyl-2-(5H)-furanone.[7]

†Stereochemistry of P-chiral phosphinylacetic acid ester—II, Part I, Ref. 3*d*.



3 1 4 6

	R'	R''	
3a	C_6H_5	CH_3	**4a**
3b	C_6H_5	C_2H_5	**4b**
3c			**4c**
3d	C_6H_5	2,4,6-/CH_3/$_3C_6H_2$	**4d**
3e	/CH_3/$_2$CH	CH_3	**4e**
3f	C_2H_5	CH_3	**4f**
3g	C_6H_5C/CH_3/$_2$	$COOCH_2CH_3$	**4g**
3h	/CH_3/$_3C$	$COOCH_2CH_3$	**4h**

Scheme 1.

Table 1. Optical rotations (c 5 CCl_4), optical purities (e.e.) and configurations of the allene esters obtained in asymmetric syntheses

2	3 R'	3 R''	ALKADIENE-1,2-CARBOXYLIC-1 ESTERS 4	$[\alpha]_D^{25}$ SOLVENT: DME-ether 1:1	C_6H_6-ether 1:1	benzene	CONFIGURATIONS *	**	***
S-/-/	3a Ph	Me	4a		-59.65° e.e. 19.2%	-50.15° e.e.16.1%	R	R	R-/-/
S-/-/	3b Ph	Et	4b	-51.4° e.e.22.8%	-35.8° e.e. 15.9%	-19.85° e.e. 8.8%	R	R	R-/-/
R-/+/ S-/-/	3c 		4c		+20.8° -17.3°	+ 7.9° - 8.1°	- -	S R	S-/+/
R-/+/ S-/-/	3d Ph	Mes	4d			- 2.0° + 1.8°	- -	S R	- -
R-/+/ S-/-/	3g $PhMe_2C$	COOEt	4g			-10.1° +11.0°	- -	R S	S-/+/
R-/+/ S-/-/	3h ^tBu	COOEt	4h			- 4.7° + 5.5°	- -	R S	S-/+/

* - Based on chemical correlation with acids 5a and 5b

** - Proposed on the basis of analysis presented in this paper

*** - Predicted from the Lowe rule

Structures of all allene derivatives isolated were confirmed by spectroscopic methods (^{1}H NMR, IR, MS). For compounds **4e**, **4g**, **5e**, **5h** the nonequivalence of diastereotopic Me groups ($\Delta\delta < 0.05$ ppm) was found by ^{1}H NMR spectra.[8]

Both enantiomers of 2,[9a] of which (−)-2 have the absolute *S* configuration,[9b,9c] and were used in asymmetric syntheses of allene esters 4. Optical rotations of the products isolated were measured immediately after purification in order to avoid errors due to decomposition. Optical rotations, as well as optical purities (e.e.) and configurations of the allene esters are summarised in Table 1.

Esters **4a** and **4b** were found to retain their optical activity during distillation *in vacuo*, because the optical rotation of the distilled and the crude products formed in the esterification of the corresponding acids with diazomethane were almost identical (see Table 2). The optical rotation of **4a** and **4b** decreased slowly even when kept at −10°, probably due to decomposition. Esters **4g** and **4h** did not change their optical activity during distillation and also retained their optical rotation when stored at room temperature for a week. On the other hand, distillation of **4d** caused complete racemisation of the optically active crude product and the results listed in Table 1 were taken on samples purified by column chromatography on silicagel. A sample of the optically active **4d** racemised at room temperature within 24 hr. For **4c** the optical rotation of only the crude product could be measured because the optical activity

Table 2. Optical rotations of acids 5a and 5b (c 5 MeOH) and the corresponding methyl esters 4a and 4b (c 5 CCl_4) of the same optical purity

	Ph, Me, H, COOR (a)	Ph, Et, H, COOR (b)
ACID R=H 5	5a +42.53° S	5b -20.34° R
OPTICAL PURITIES	13.4%	9.1% *
ESTER crude	+40.80°	-20.45°
R=Me 4 distilled	4a +41.80° S	4b -20.45° R

* - based on the results of lactonisation[7].

rapidly decreased during purification. There was no doubt that **4c** was the only optically active component in this mixture because within 5 days the sample became optically inactive and no other chiral contaminants were present. All attempts at preparing the optically active **4e** failed.

In order to find the optical purity of ester **4a** obtained in the asymmetric synthesis, alkaline hydrolysis of this material was attempted. Unfortunately, only racemic acid **5a** was isolated. This result was interpreted in terms of racemisation of the allene system under basic conditions. When NaOD-D_2O solution was employed in the hydrolysis, 2-deuterio-4-phenylbuta-2,3-dienoic acid (**5aD**) was formed as the only product. This indicates that H–D exchange of allenic hydrogen had occured. The intermediacy of allenyl carbanions in this hydrolysis (Scheme 2), followed by racemisation, seems to be a reasonable explanation for the results.[10]

Optical purity of **4a** and **4b** was ascertained in the following way. Racemic acids **5a** and **5b** were partially resolved[3c,5b] and samples of known optical purity[5b,7] (Table 2) were transformed into the corresponding esters **4a** and **4b** with equimolar amounts of ethereal diazomethane. The optical purity of the esters are the same as those of the acids because esterification caused no change in the asymmetry of the allene system. On the basis of the results presented in Table 2, optical purity (e.e.) of esters **4a** and **4b** were calculated (Table 1). The optical purity was higher in those cases when reactions were carried out in more polar solvents.

Data listed in Table 2 also allowed us to assign the absolute configurations of the esters **4a** and **4b** because the *S* configuration of the corresponding dextrorotatory acids **5a** and **5b** had been determined earlier.[5b] Dextrorotatory esters **4a** and **4b** have also the absolute *S* configuration. On the other hand, the absolute configurations of allene carboxylic acids could be predicted by the Lowe rule.[11] Taking into account the fact that the optical rotation of the acids and the corresponding esters of the same optical purity are close together (Table 2), the assumption that the polarisibility of the carboxy and carbomethoxy groups are of the same order is reasonable. The Lowe rule could therefore be applied to the other optically active allene esters discussed in this paper (Table 1). This procedure failed in the case of ester **4d** because data on the relative polarisibility of two aromatic substuents was not available.

The mechanism of the Horner–Emmons reaction of phosphonate carbanions with ketenes has not been investigated, despite the fact that numerous papers dealing with the synthesis of allene derivatives in this way have appeared.[3] For this reason it was assumed that the mechanism of the reaction discussed is analogous to that of carbonyl compounds with stabilised phosphonate carbonions[12] and involves (i) nucleophilic addition of carbanion **1** to the CO group of ketene forming enolate anion **7**, and (ii) *cis*-elimination of sodium O-methylphenylphosphonate (**6**) from **7** leading finally to the allene carboxylic ester **4** (Scheme 3).

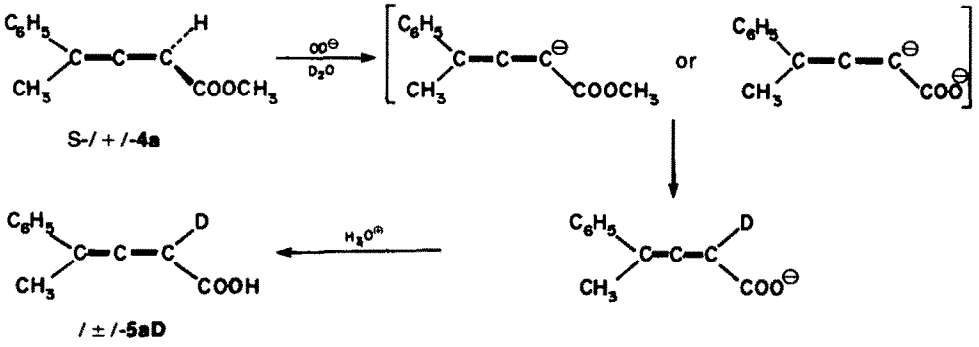
No kinetic data are available for the reaction studied in this paper. Following again the generally accepted mechanism of the reaction of the stabilised phosphonate carbanions with carbonyl compounds,[12] *cis*-elimination of **6** could be considered to be the kinetically important step ($k_2 < k_{-1}$). It has been postulated that in the elimination step of the Horner–Emmons reaction, species containing the 4-membered oxaphosphetane ring (**9**) are involved as intermediates or as transition states. Such species are of crucial importance in the interpretation of results observed; but no evidence had been presented for their actual existence.

As shown in Table 1 and in Scheme 3, (*R*)-(−)-**4a** as well as **4b** were produced from the carbanion (*S*)-(−)-**1**. Consequently the elimination step may be considered in terms of nonbonding and electronic effects in diastereoisomeric intermediates or transition states (**8**).

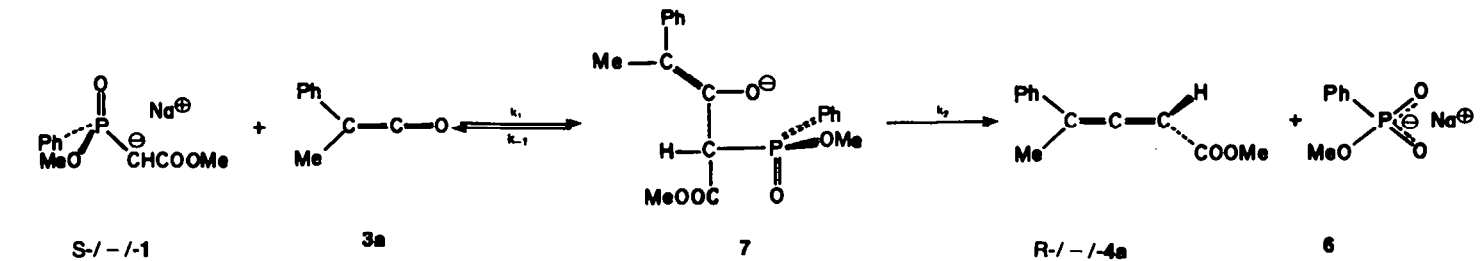
Four diastereoisomeric enolate anions **7** could be produced in the first step of the reaction. Only two of them (**7A** and **7D**) will yield the allene ester with the absolute configuration observed in the experiment. In the case of the phosphonate studied, three kinds of species **9a–c** with different orientations of substituents around the *P* atom in a trigonal bipyramid are possible (Fig. 1).

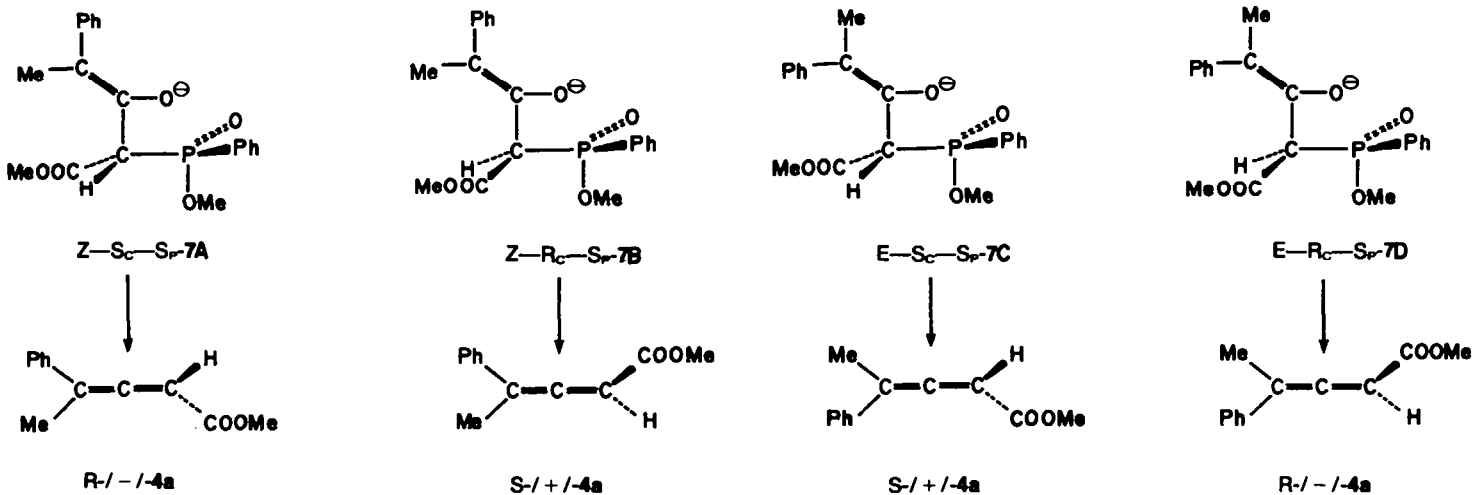
Examination of these structures from the point of view of relative apicophilicity[13] shows that **9a** is more stable than **9b** and **9c**. In **9a** the 4-membered ring occupies the apical-equatorial position with O in the apical and C in the equatorial positions. The other favorable orientations around the *P* atom in **9a** involve an equatorial oxide anion and phenyl group (both of low apicophilicity) and an apical OMe group (highly preferable orientation). In the transition states **9b** and **9c** two substituents are oriented in unfavorable positions, making the activation energies higher than that for **9a**.

Application of these conclusions to the *cis*-elimination of **6** from **7A** leads us to postulate **8A–a** as the transition state of lowest activation energy in this process (Fig. 2). As shown in the Newman projection, nonbonding inter-



Scheme 2.





Scheme 3.

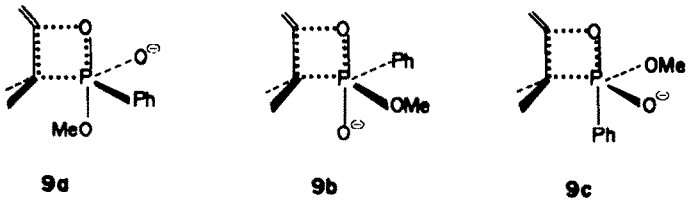


Fig. 1.

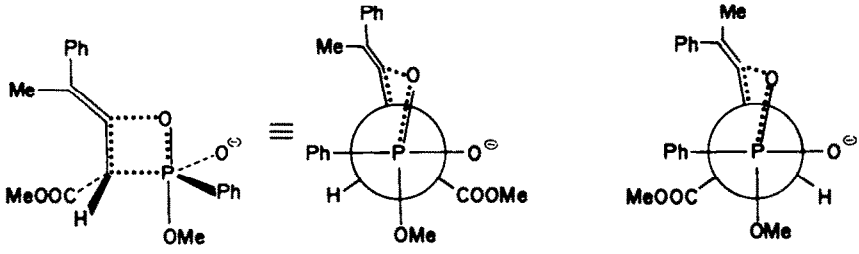


Fig. 2.

actions of bulky substituents in **8A–a** are minimised in comparison with those in **8D–a**, which would compete as an alternative transition state leading also to an excess of (*R*)-(−)-**4a**.

Favourable orientations of all substituents around the pentavalent *P* atom and minimised repulsions of the bulky substituents would require less energy to attain the transition state **8A–a** than in the other orientations of the substituents, so consequently, a considerable excess of (*R*)-(−)-**4a** over the *S* enantiomer would be produced. The same will apply to the homologous ester **4b**. Similar analysis allowed us to propose absolute configurations for the other optically active allene carboxylic esters obtained from **1** and selected ketenes (Table 1). These assignments are in full agreement with configurations predicted by the Lowe rule.

EXPERIMENTAL†

Solvents and starting materials. All solvents were purified by methods described in the literature and distilled under argon before use. Literature procedures were followed for the preparation of (+) and (−)-**2**[9a] and ketenes: **3a**[3b,6a–c], **3b**[6c,6d], **3d**[6e], **3g**[6f], **3h**[6f] and **3c**.[6b] Based on the Duckworth method[6c] **3e** and **3f** ketenes were synthesised using the corresponding malonic acid, trifluoroacetic anhydride and pyridine; (**3e**, 24–44%); b.p. 80–81°; NMR(CCl_4): 1.05 (d, 6H, $^3J = 6.6$, $(CH_3)_2C$), 1.58 (s, 3H, CH_3C=), 2.20 (sp, 1H, $^3H = 6.6$, $\underline{H}C(CH_3)_2$); IR (film): 2150 $\nu_{C=C=O}$; (**3f**, 18%); b.p. 40° ((lit.[14] −26 to −28°) (12 mm); NMR (CCl_4): 1.05 (t, 3H, $^3J = 7.0$, $\underline{CH_3}$-CH_2), 1.60 (s, 3H, CH_3C=), 2.00 (q, 2H, $^3J = 7.0$, $\underline{CH_2}$-CH_3); IR (film): 2160 $\nu_{C=C=O}$.

Synthesis of 4,4-disubstituted Methyl alka-2,3-dienoates (**4**)

General procedure. To NaH (0.48 g, 0.02 mol) suspended in 20 ml benzene (or benzene–ether 1:1, or DME-ether 1:1), (+) or (−)-**2** (4.58 g, 0.02 mol) dissolved in 20 ml of an appropriate solvent was added dropwise with stirring at 5°. The soln was stirred at room temp until evolution of gas ceased. To the soln of **1** obtained, 0.02 mol of the ketene dissolved in 30 ml of the solvent was added dropwise at 5–7°. Stirring was continued below 10° for 3 hr. To the cooled mixture 50 ml water was added and also 100 ml benzene when DME had been used as cosolvent. The water layer was extracted with ether (3 × 25 ml). The combined organic layers were washed with water, dried and evaporated. Column chromatography on silicagel (100–200 mesh) using benzene as eluant was employed and the crude products **4a–4h** free from the starting ester **2** were distilled *in vacuo* to give analytically pure samples.

Methyl 4-phenylpenta-2,3-dienoate (**4a**), yield 41%; b.p. 105–10° (bath) (0.05 mm) lit.[5a] 70° (0.1 mm); NMR (CCl_4): 2.10 (d, 3H, $^5J = 2.9$, CH_3C=), 3.56 (s, 3H, CH_3OOC), 5.80 (q, 1H, $^5J = 2.9$, HC=C=C), 7.0–7.5 (m, 5H, C_6H_5); IR (film): 1940 $\nu_{C=C=C}$, 1720 $\nu_{C=O}$; MS: 188 (M^+) (100%). (Found: C, 76.31; H, 6.55. Calc. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%).

Methyl 4-phenylhexa-2,3-dienoate **4b**), yield 42%; b.p. 110–15° (bath) (0.1 mm) lit[3c] 90–4° (0.05 mm); m.p. 41–2° (lit.[3c] 41–2°); NMR (CCl_4): 1.08 (t, 3H, $^3J = 7.1$, CH_3CH_2), 2.50 (dq, 2H, $^3J = 7.1$, $^5J = 2.1$, CH_2CH_3), 3.58 (s, 3H, CH_3OOC), 5.85 (t, 1H, $^5J = 2.1$, HC=C=C), 7.0–7.5 (m, 5H, C_6H_5); IR (film): 1940 $\nu_{C=C=C}$, 1720 $\nu_{C=O}$; MS: 202 (M^+) (41%). (Found: C, 77.35; H, 7.05. Calc. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%).

Crude 1-(3-*carbomethoxypropadiene*)-1,2,3,4-*tetrahydronaphthalene* (**4c**), NMR (CCl_4): 1.7–2.1 (m, 2H) and 2.3–2.8 (m, 4H) -$CH_2CH_2CH_2$, 3.54 (s, 3H, CH_3OOC), 5.84 (t, 1H, $^5J = 3.0$, HC = C=C). 7.1–7.7 (m, 4H, C_6H_4); IR (film): 1930 $\nu_{C=C=C}$, 1715 $\nu_{C=O}$.

Methyl 4-mesityl-4-phenylbuta-2, 3-dienoate (**4d**), yield 72%; b.p. 170–2° (bath) (0.1 mm); m.p. 64–65°; NMR (CCl_4): 2.63 (s, 6H, CH_3 *o*-), 2.78 (s, 3H, CH_3 *p*-), 4.12 (s, 3H, CH_3OOC), 6.35 (s, 1H, HC = C = C), 7.25 (s, 2H, C_6H_2-mesityl), 7.5–7.7 (m, 5H, C_6H_5); IR (film): 1940 $\nu_{C=C=C}$, 1735 $\nu_{C=O}$; MS: 292 (M^+) (51%). (Found: C, 82.15; H, 6.89. Calc for $C_{20}H_{20}O_2$: C, 82.16, H, 6.90%).

Methyl 4,5-dimethylhexa-2, 3-dienoate (**4e**, yield 13%; (b.p. 43°) 1 mm; NMR (CCl_4): 1.05 (d, 6H, $^3J = 6.5$, $(CH_3)_2C$), 1.77 (d, 3H, $^5J = 2.7$, CH_3C=), 2.20 (dsp, 1H, $^3J = 6.5$, $^5J = 2.7$, $(CH_3)_2\underline{C}HC$=), 3.62 (s, 3H, $CH_3O\underline{O}C$), 5.41 (qu, 1H, $^5J = 2.7$, HC=C=C); IR (film): 1970 $\nu_{C=C=C}$, 1730 $\nu_{C=O}$; MS: 154 (M^+) (2.7%). (Found: C, 69.70; H, 9.40. Calc. for $C_8H_{11}O_2$: C, 70.10; H, 9.15%).

Methyl 4-methylhexa-2, 3-dienoate (**4f**), yield 4%; b.p. 50° (bath) (1 mm) lit.[5a] 68–9° (9 mm); NMR (CCl_4): 0.89 (t, 3H, $^3J = 7.1$, $\underline{CH_3}CH_2$), 1.49 (d, 3H, $^5J = 2.9$, CH_3C=), 1.7 (dq, 2H,

†General analytical procedures and instrumentation were the same as described in the previous paper.[7] Solutions of ketenes were transferred with syringes. All experiments with ketenes were carried out under dry argon.

$^3J = 7.1$, $^5J = 2.9$, $\underline{CH_2}CH_3$), 3.43 (s, 3H, CH_3OOC), 5.64, (sx, 1H, $^5J = 2.9$, HC=C=C); IR (film): 1950 $\nu_{C=C=C}$, 1725 $\nu_{C=O}$.

3-*Carboethoxy*-1-*carbomethoxy*-4-*methyl*-4-*phenylpenta*-1, 2-*diene* (**4g**) yield 59% (b.p. 119–22°) 0.2 mm; NMR (CCl_4): 1.02 (t, 3H, $^3J = 7.0$, $\underline{CH_3}CH_2O$), 1.52 (s, 3H, $\underline{CH_3}(CH_3)C$), 1.55 (s, 3H, $CH_3(\underline{CH_3})C$), 3.70 (s, 3H, CH_3OOC), 3.86 (q, 2H, $^3J = 7.0$, $CH_3\underline{CH_2}$), 5.90 (s, 1H, HC=C=C), 6.7–7.4 (m, 5H, C_6H_5); IR (film): 1940 $\nu_{C=C=C}$, 1730 $\nu_{C=O}$; MS: 288 (M^+) (0.32%). (Found: C, 70.57; H, 7.11. Calc. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99%).

3-*Carboethoxy*-1-*carbomethoxy*-4, 4-*dimethylpenta*-1, 2-*diene* (**4h**), yield 80%; (b.p. 68–70°) 0.5 mm; NMR (CCl_4): 1.20 (s, 9H, $(CH_3)_3C$), 1.25 (t, 3H, $^3J = 7.5$, $\underline{CH_3}CH_2O$), 3.74 (s, 3H, CH_3OOC), 4.20 (q, 2H, $^3J = 7.5$, $CH_3\underline{CH_2}O$), 5.79 (s, 1H, HC=C=C); IR (film): 1955 $\nu_{C=C=C}$, 1715 $\nu_{C=O}$; MS: 226 (M^+) (0.68%). (Found: C, 63.81; H, 8.12. Calc. for $C_{12}H_{18}O_4$: C, 63.69; H, 8.01%).

Synthesis of 4, 4-*disubstituted alka*-2, 3-*dienoic acids* (**5**)

General procedure. A mixture of **4a, b, d, g, h** (5 g), 5 ml 30% NaOH and 5 ml MeOH was refluxed for 2 hr. Most of the MeOH was evaporated, then water (70 ml) was added to the residue and the water layer was extracted with ether (4 × 30 ml). The aqueous soln was cooled to −10° and slowly acidified with 10% H_2SO_4. The crude acids(**5a, b, d, g, h** were extracted with ether, and the extracts washed with brine and dried. Solvents were removed and the crude products were purified by crystallisation or column chromatography.

4-*Phenylpenta*-2, 3-*dienoic acid* (**5a**), yield 20%; m.p. 116–8° (benzene–hexane, 1:4), lit[3c] 115–7° and [6d] 120–1°); NMR (acetone-d_6): 2.18 (d, 3H, $^5J = 3.0$, $CH_3C=$), 5.86 (q, 1H, $^5J = 3.0$, HC=C=C), 7.1–7.5 (m, 5H, C_6H_5); IR (KBr): 1950 $\nu_{C=C=C}$, 1670 $\nu_{C=O}$; MS: 174 (M^+) (100%). (Found: C, 75.85; H, 5.79, Calc. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79%).

4-*Phenylhexa*-2, 3-*dienoic acid* (**5b**), yield 20%; m.p. 103–4° (benzene), (lit.[3b] 100–1°); NMR (acetone-d_6): 1.14 (t, 3H, $^3J = 7.3$, $\underline{CH_3}CH_2C=$), 2.55 (dq, 2H, $^3J = 7.3$, $^5J = 3.4$, $CH_3\underline{CH_2}C=$), 5.96 (t, 1H, $^5J = 3.4$, HC=C=C), 7.2–7.5 (m, 5H, C_6H_5); IR (KBr): 1960 $\nu_{C=C=C}$, 1685 $\nu_{C=O}$; MS: 188 (M^+) (42.5%). (Found: C, 76.70; H, 6.56, Calc. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%).

4-*Mesityl*-4-*phenylbuta*-2, 3-*dienoic acid* (**5d**), yield 50%; m.p. 174–5° (benzene–hexane, 1:2 or EtOH–H_2O, 3:1); NMR (acetone-d_6): 2.62 (s, 6H, CH_3 *o*–), 2.77 (s, 3H, CH_3 *p*–), 5.37 (s, 1H, HC=C=C), 7.27 (s, 2H, C_6H_2-mesityl), 7.65–7.85 (m, 5H, C_6H_5); IR (KBr): 1960 $\nu_{C=C=C}$, 1690 $\nu_{C=O}$; MS: 278 (M^+) (100%). (Found: C, 82.05; H, 6.54, Calc. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.51%).

4-*Methyl*-4-*phenylpenta*-1, 2-*diene*-1, 3-*dicarboxylic acid* (**5g**), yield 71%; m.p. 169–70° (dec) (hexane–ether, 3:2); NMR (acetone-d_6): 1.55 (s, 6H, $(CH_3)_2C$), 6.10 (s, 1H, HC=C=C), 7.05–7.55 (m, 5H, C_6H_5); IR (KBr): 1950 $\nu_{C=C=C}$, 1690 $\nu_{C=O}$; MS: 245 (M^+) (0.13%). (Found: C, 68.09; H, 5.72. Calc. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.72%).

4, 4-*Dimethylpenta*-1, 2-*diene*-1, 3-*dicarboxylic acid* (**5h**), yield 66%; m.p. 174–5° (dec) (benzene–acetone, 10:1); NMR (acetone-d_6): 1.15 (s, 9H, $(CH_3)_3C$), 5.90 (s, 1H, HC=C=C); IR (KBr): 1940 $\nu_{C=C=C}$, 1690 $\nu_{C=O}$; MS: 184 (M^+) (0.20%). (Found: C, 58.52; H, 6.40. Calc. for $C_9H_{12}O_4$: C, 58.68; H, 6.56%).

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