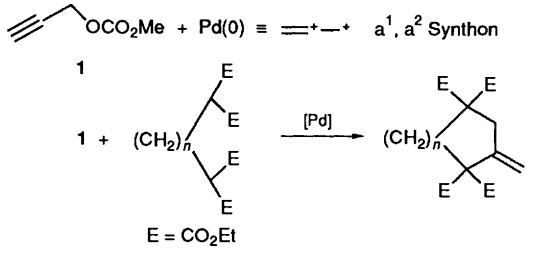
Prop-2-ynylic Carbonates as a^1,a^2 Synthons in Palladium Catalysed Annulation Reactions with Bifunctional Nucleophiles

Lifeng Geng and Xiyan Lu *
Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

Prop-2-ynylic carbonates were used as a^1,a^2 synthons in palladium catalysed annulation reactions with bifunctional nucleophiles. Methods were developed for the synthesis of 3-methylenedihydropyran derivatives and methylenecycloalkane derivatives in good yields. The regiochemistry of such reactions is discussed based upon the proposed mechanism.

Methylenecyclic compounds are a class of important compounds in natural product chemistry.[1] Due to their widespread occurrence in nature, methylene-cyclopentane, -cyclohexane and -cycloheptane derivatives have attracted much attention and major efforts have been devoted to their synthesis.[2] Among the organometallic complex catalysed cyclization strategies,[3] a powerful example is the palladium(0) complex catalysed trimethylenemethane (TMM) cycloaddition reaction.[4]

The reactions of triple bonds have attracted much attention in recent years. Prop-2-ynylic halides, alcohols, and their derivatives react with organocopper reagents to give substituted allenes.[5] Furthermore, organomagnesium or zinc reagents react with prop-2-ynylic compounds in the presence of a palladium,[6] copper[7] or nickel[8] catalyst. Tsuji *et al.* reported that prop-2-ynylic carbonates react with soft carbon nucleophiles catalysed by palladium(0) complex and a method for the synthesis of furan derivatives was developed.[9] In Tsuji's reaction, prop-2-ynyl carbonate **1** could accept the attack of two molecules of nucleophile. It occurred to us that in the presence of palladium(0) complex, **1** could act as a a^1,a^2 synthon which could accept the attack of bifunctional nucleophiles to accomplish a new type of annulation methodology.

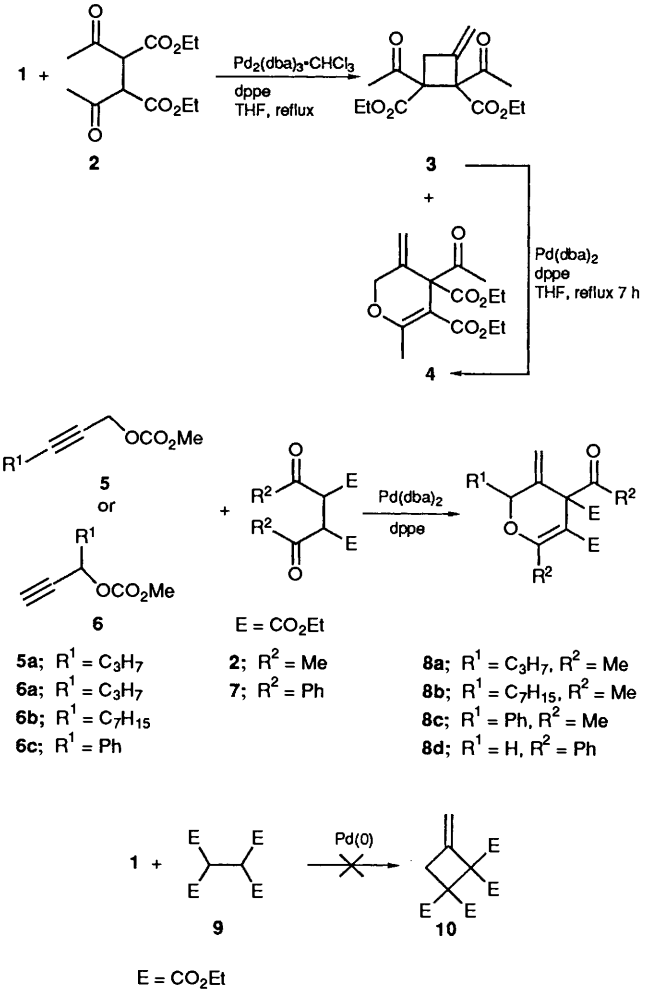


Here we wish to report our results of the palladium catalysed annulation reactions of prop-2-ynylic carbonates and bifunctional nucleophiles for the synthesis of methylenecycloalkane derivatives.

Results and Discussion

Diethyl 2,3-diacetylsuccinate **2** was firstly used as a 1,2-dinucleophile in a reaction with prop-2-ynyl carbonate **1** catalysed by Pd(0) complex. Besides the expected methylene-cyclobutane derivative **3**, an unexpected 3-methylenedihydropyran derivative **4** which is due to the carbon, oxygen attack, was obtained. The preliminary results have been published in a communication.[10] When substituted prop-2-ynylic carbonates **5** or **6** were used, only the 3-methylenedihydropyran derivative **8** was obtained in good yield.[10]

In order to avoid *O*-alkylation of the dinucleophile **2**,

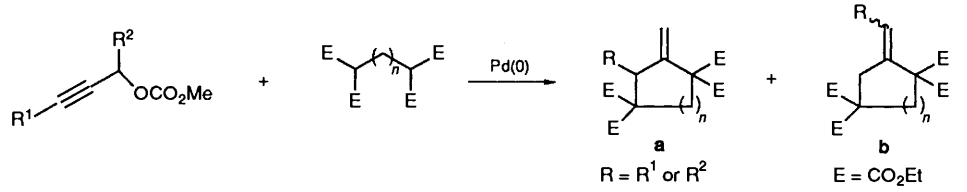


compound **9** was used as a 1,2-dinucleophile to react with **1**, but the reaction failed to take place and the desired four membered ring product **10** could not be obtained.

Furthermore, the reactions of prop-2-ynylic carbonates **1**, **5** and **6** with 1,3-, 1,4- and 1,5-dinucleophiles gave the corresponding methylene-cyclopentanes, -cyclohexanes and -cycloheptanes as shown in Table 1.

From Table 1, it can be seen that when the isomeric prop-2-ynylic carbonates **5a** or **6a** were allowed to react with **11** or **15**, a mixture of products with the same ratio of **14a**:**14b** or **17a**:**17b** was obtained, respectively. These results confirmed that the reaction intermediate was a π-allylic palladium complex.[9] It is interesting to note that the regiochemistry of five- and six-membered rings is different. For six membered ring products **17**,

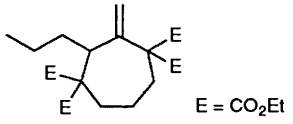
Table 1 Reactions of prop-2-ynylic carbonates with dinucleophiles[a]



Prop-2-ynylic carbonate			Dinucleophile		Time	Isolated	Product		
No.	R^1	R^2	No.	*n*	*t*/h	yield (%)	No.	R	Ratio of **a**/**b**[b]
1	H	H	**11**	1	4	70	**12**	H	—
6b	H	C_7H_{15}	**11**	1	15	45	**13**	C_7H_{15}	19/1
5a	C_3H_7	H	**11**	1	7	65	**14**	C_3H_7	9/1
6a	H	C_3H_7	**11**	1	15	41	**14**	C_3H_7	9/1
1	H	H	**15**	2	12	69	**16**	H	—
5a	C_3H_7	H	**15**	2	29	93	**17**	C_3H_7	1/3
6a	H	C_3H_7	**15**	2	28	82	**17**	C_3H_7	1/3
18	C_4H_9	H	**15**	2	28	82	**19**	C_4H_9	1/4
6b	H	C_7H_{15}	**15**	2	50	66	**20**	C_7H_{15}	1/2.3
1	H	H	**21**	3	20	65	**22**	H	—
5a	C_3H_7	H	**21**	3	20	80	**23**	C_3H_7	only **b**
6a	H	C_3H_7	**21**	3	48	86	**23**	C_3H_7	only **b**

[a] The reactions were carried out at 80 °C under the catalysis of $Pd(dba)_2$ and dppe. [d] Determined by ^1H NMR spectroscopy.

19 and **20**, the main product **17b**, **19b** and **20b** was the one with the substituent on the double bond. For seven membered rings, **5a** or **6a** reacted with **21** and gave only **23b**, no other possible product **23a** was detected.



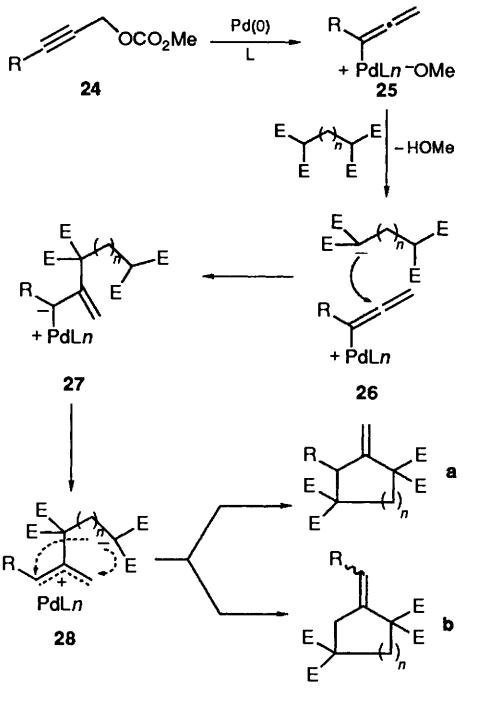
23a

The mechanism of this palladium catalysed annulation reaction may be similar to that of Tsuji's reaction[9] and is speculated as shown in Scheme 1.

The initial step is an S_N2' reaction of the palladium–phosphine complex with **24** and subsequent decarboxylation to give (propa-1,2-dienyl)palladium complex **25**. The methoxide anion then captures an acidic hydrogen from the nucleophile to give complex **26**. Next, the carbanion of the nucleophile attacks the C(2)-carbon of the propa-1,2-dienyl moiety to form the carbene complex **27** which picks up another active hydrogen from the nucleophile moiety to give the π-allyl palladium complex **28**. Intramolecular attack of the carbanion onto the π-allylpalladium moiety of **28** gave **a** and **b**. It is clear that the last step determines the regiochemistry of the annulation reaction. If the carbanion in **28** attacks the more substituted side of π-allylpalladium moiety, the product is **a**, otherwise **b** is obtained. From our results, it is concluded that the size of the ring formed controls the regiochemistry of this reaction.

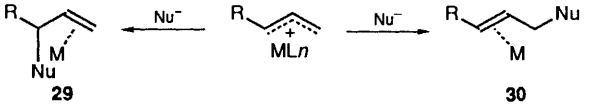
In palladium(0) catalysed allylation reactions, nucleophiles in general attack on the less-hindered carbon of the π-allyl palladium complex.[11] But in molybdenum and tungsten complex catalysed allylation reactions, nucleophiles attack the more hindered side of the π-allylmetal complexes.[12] In this type of reaction, steric and electronic effects may operate in opposite directions.

A dominant electronic effect in the transition state of this reaction leads to reactions at the more hindered side of the π-allylpalladium complex, but a dominant steric effect in the transition state leads to reactions at the less hindered side. The



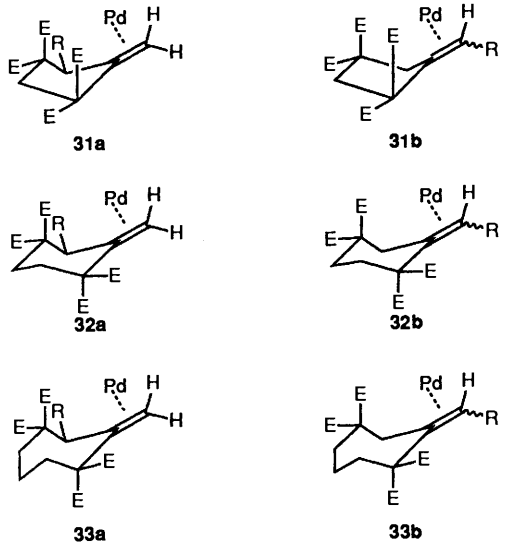
Scheme 1

steric effect controls the palladium(0) catalysed allylation reactions. For molybdenum and tungsten complex catalysed reactions the kinetic effect is more important.



Examining the kinetic products **29** and **30**, steric and electronic factors with respect to olefin–metal(0) complexation should favour the formation of **29**. So the molybdenum and

tungsten complex catalysed allylation reactions prefer attack at the more hindered side of the π-allylmetal complex. Based upon these considerations, the regiochemistry of our annulation reactions may be speculated upon, based on a combination of steric and electronic effects.



In the formation of the five membered ring,[13] the steric effects of the two axial CO_2Et groups are similar in both of the transition states leading to products **31a** and **31b**. Thus the effects on the transition states become less important for determining the distribution of the regiochemistry while the kinetic effect becomes more important. The preferred kinetic complexation of **31a** made nucleophilic attack on the more hindered side preferable, and **31a** was obtained as the major product. This result is consistent with the five membered ring closure reactions formed by [3 + 2] cycloaddition.[14]

In the six membered ring[15] formation reaction, the difference in steric effects of the two transition states leading to **32a** and **32b** becomes larger compared with those of the five membered ring formation reaction, so that the steric effects dominated the reaction and normal attack at the less hindered side took place, meanwhile the influence of the kinetic complexation decreased. In the procedure for the seven membered ring closure reaction, steric effects in the transition state dominated and the products were almost entirely **33b**.

Experimental

All reactions were carried out under N_2 using Schlenk techniques. Prop-2-ynylic carbonate,[9] diethyl 2,3-diacetylsuccinate **2**,[16] diethyl 2,3-benzoylsuccinate **7**,[16] $(EtO_2C)_2CH(CH_2)_nCH(CO_2Et)_2$ (n = 1,2,3)[17] were prepared according to published methods.

IR spectra were recorded on a IR-440 spectrometer or a Perkin-Elmer 983 spectrometer. ^1H NMR spectra were recorded on a EM-360A spectrometer or a FX-90Q spectrometer or a AZ-300 MHz spectrometer. Unless otherwise specified, ^1H NMR spectra were recorded in CCl_4 at 60 MHz, J values are given in Hz. Mass spectra were recorded on a Finnigan 4021 spectrometer. Light petroleum refers to the fraction of b.p. 60–90 °C.

Reaction of Compounds **1** *and* **2**.—A mixture of $Pd_2(dba)_3$·$CHCl_3$ (26 mg, 0.025 mmol), dppe (40 mg, 0.1 mmol) and THF (5 cm^3) was stirred until the solution became orange in colour. Compound **2** (258 mg, 1.0 mmol) was added by syringe and then compound **1** (150 mg, 1.3 mmol) was added to the mixture which was then heated at reflux for 7 h until the reaction was complete, as monitored by TLC. The reaction mixture was adsorbed on silica gel and evaporated to dryness. The silica gel was eluted with ether. The ether solution was evaporated and the residual oil was separated by preparative TLC (silica gel, ethyl acetate–light petroleum, 1:10). Compounds **3** (140 mg, 52%) and **4** (120 mg, 45%) were obtained.

Diethyl 1,2-*diacetyl*-3-*methylenecyclobutane*-1,2-*dicarboxylate* **3**, $\delta_H(CCl_4$; 60 MHz) 1.22 (6 H, t), 2.30 (6 H, s), 3.90–4.20 (4 H, m,), 4.30 (2 H, s), 5.23 (1 H, s) and 5.32 (1 H, s); ν_{max}(neat)/cm^{-1} 1740 (C=O), 1720 (C=O) and 1620 (C=C); m/z 297 (M + 1)$^+$, 252, 224, 209 (base) and 179 (Found: C, 61.2; H, 6.5. $C_{15}H_{20}O_6$ requires C, 60.80; H, 6.80%).

Diethyl 4-*acetyl*-3,4-*dihydro*-6-*methyl*-3-*methylene*-2H-*pyran*-3,4,5-*dicarboxylate* **4**, $\delta_H(CCl_4$; 60 MHz) 1.25 (6 H, t), 1.43 (3 H, s), 2.23 (3 H, s), 3.85–4.23 (4 H, m), 4.38 (2 H, m), 5.08 (1 H, m) and 5.30 (1 H, m); ν_{max}(neat)/cm^{-1} 1725 (C=O), 1705 (C=O) and 1625 (C=C); m/z 297 (M^+), 251 (base), 223 and 208 (Found: C, 60.7; H, 6.85. $C_{15}H_{20}O_6$ requires C, 70.80; H, 6.80%).

Conversion of Compound **3** *to* **4**.—A mixture of $Pd(dba)_2$ (5 mg), dppe (10 mg) and **3** (30 mg) and THF (2 cm^3) was stirred and heated at reflux for 7 h. Compound **4** (10 mg, 33%) was isolated by preparative TLC (eluent: ethyl acetate–light petroleum, 1:10). The unchanged part of the mixture was recovered as compound **3**.

General Procedure for the Preparation of 3-*Methylenedihydropyran Derivatives*.—A mixture of $Pd(dba)_2$ (30 mg, 0.05 mmol), dppe (40 mg, 0.1 mmol) and THF (5 cm^3) was stirred until the solution became orange. Then compound **2** (258 mg, 1.0 mmol) and prop-2-ynylic carbonates (1.3 mmol) were added by syringe. The reaction mixture was heated at reflux until the reaction was complete as monitored by TLC. The products were isolated by preparative TLC.

Diethyl 4-*acetyl*-3,4-*dihydro*-6-*methyl*-3-*methylene*-2-*propyl*-2H-*pyran*-4,5-*dicarboxylate* **8a** (eluent: ethyl acetate–light petroleum, 1:15); δ_H 0.83–1.53 (16 H, m), 2.18 (3 H, s), 4.03 (4 H, q), 4.40–4.73 (1 H, m), 4.90 (1 H, m) and 5.30 (1 H, m); ν_{max}(neat)/cm^{-1} 1750 (C=O), 1710 (C=O) and 1650 (C=C); m/z 339 (M + 1)$^+$, 293, 265, 250 (base) and 177 (Found: C, 63.95; H, 7.8. $C_{18}H_{26}O_6$ requires C, 63.89; H, 7.74%).

Diethyl 4-*acetyl*-2-*heptyl*-3,4-*dihydro*-6-*methyl*-3-*methylene*-2H-*pyran*-4,5-*dicarboxylate* **8b** (eluent: ethyl acetate–light petroleum, 1:20); δ_H 0.33–1.52 (24 H, m), 2.10 (3 H, s), 4.08 (4 H, q), 4.38–4.68 (1 H, m), 4.95 (1 H, m) and 5.33 (1 H, m); ν_{max}(neat)/cm^{-1} 1745 (C=O), 1710 (C=O) and 1650 (C=C); m/z 395 (M + 1)$^+$ (base), 349 and 306 (Found: C, 66.7; H, 8.8. $C_{22}H_{34}O_6$ requires C, 66.97; H, 8.68%).

Diethyl 4-*acetyl*-3,4-*dihydro*-6-*methyl*-3-*methylene*-2-*phenyl*-2H-*pyran*-4,5-*dicarboxylate* **8c** (eluent: ethyl acetate–light petroleum, 1:40); δ_H 1.10–1.40 (6 H, m), 1.70 (3 H, s), 1.85 (3 H, s), 3.90–4.30 (4 H, m), 5.10 (1 H, m), 5.57 (2 H, m) and 7.23 (5 H, m); ν_{max}(neat)/cm^{-1} 1745 (C=O), 1710 (C=O) and 1650 (C=C); m/z 373 (M + 1)$^+$, 327 (base), 299 and 284 (Found: C, 66.95; H, 6.4. $C_{21}H_{24}O_6$ requires C, 67.73; H, 6.50%).

Reaction of Compounds **7** *and* **1**.—A mixture of $Pd(dba)_2$ (15 mg, 0.025 mmol), dppe (20 mg, 0.05 mmol), compound **7** (191 mg, 0.5 mmol) and 1,4-dioxane (2 cm^3) was stirred until the solution became orange. Acetonitrile (2 cm^3) was added and compound **1** (75 mg, 0.65 mmol) was added by syringe. The reaction mixture was heated at 100 °C for 47 h. The product was isolated by preparative TLC (eluent: ethyl acetate–light petroleum, 1:15). *Diethyl* 4-*benzoyl*-3,4-*dihydro*-3-*methylene*-6-*phenyl*-2H-*pyran*-4,5-*dicarboxylate* **8d** (160 mg, 76%) was

obtained as a white solid, m.p. 109 °C; δ_H 0.80 (3 H, t), 1.19 (3 H, t), 3.50 (2 H, q), 4.10 (2 H, q), 4.71 (2 H, m), 5.28 (1 H, m), 5.43 (1 H, m) and 7.20–8.10 (10 H, m); ν_{max}(KBr)/cm^{-1} 1740 (C=O), 1685 (C=O), 1630 (C=C) and 1490; *m/z* 421 (M + 1)$^+$, 374, 345, 315, 105 (base) and 77 (Found: C, 71.85; H, 5.75. $C_{25}H_{24}O_6$ requires C, 71.42; H, 5.92%).

General Procedure for the Synthesis of Methylenecyclopentane Derivatives.—A mixture of Pd(dba)$_2$ (30 mg, 0.05 mmol), dppe (40 mg, 0.10 mmol) and THF (2.5 cm^3) was stirred to become orange. Acetonitrile (2.5 cm^3) was added, then compound **11** (330 mg, 1.0 mmol) and prop-2-ynylic carbonates (1.3 mmol) were added by syringe. The reaction mixture was heated at 80 °C until the reaction was complete. The product was isolated by flash column chromatography.

Tetraethyl 5-methylenecyclopentane-1,1,3,3-tetracarboxylate **12**, δ_H 1.20 (12 H, t), 3.04 (4 H, s), 4.10 (8 H, q) and 5.30 (2 H, m); ν_{max}(neat)/cm^{-1} 1731 (C=O) and 1444 (C=C); *m/z* 371 [(M + 1)$^+$, base], 325, 297, 251, 223, 179, 105 and 79 (Found: C, 57.85; H, 7.25. $C_{18}H_{26}O_8$ requires C, 58.37; H, 7.07%).

Tetraethyl 4-heptyl-5-methylenecyclopentane-1,1,3,3-tetracarboxylate **13a** *and tetraethyl 5-octylidenecyclopentane-1,1,3,3-tetracarboxylate* **13b** were isolated as a mixture, the ratio of which was determined according to the olefin proton absorption in ^{1}H NMR spectrum (9:1); ν_{max}(neat)/cm^{-1} 1732 (C=O) and 1646 (C=C); *m/z* 413 [(M + 1)$^+$], 368, 339, 292 (base), 265, 219 and 119 (Found: C, 60.85; H, 8.1. $C_{21}H_{32}O_8$ requires C, 61.15; H, 7.82%); δ_H(CDCl$_3$; 300 MHz) **13a** 0.8 (3 H, m), 1.17–1.53 (16 H, m), 3.00–3.20 (3 H, m), 4.20 (8 H, m), 5.31 (d, 1 H, *J* 1.4), 5.47 (d, 1 H, *J* 1.4); **13b** 0.8 (3 H, m), 1.17–1.53 (18 H, m), 3.00–3.20 (2 H, m), 4.20 (8 H, m) and 5.61 (1 H, t).

Tetraethyl 5-methylene-4-propylcyclopentane-1,1,3,3-tetracarboxylate **14a** *and tetraethyl 5-butylidenecyclopentane-1,1,3,3-tetracarboxylate* (19:1); ν_{max}(neat)/cm^{-1} 1734 (C=O) and 1463 (C=C); *m/z* 469 [(M + 1)$^+$], 423, 395, 348 (base), 275, 247 and 105 (Found: C, 63.7; H, 8.85. $C_{25}H_{40}O_8$ requires C, 64.08; H, 8.60%); δ_H(CDCl$_3$; 300 MHz) **14a** 0.87 (3 H, t), 1.03–1.48 (24 H, m), 2.99–3.21 (3 H, m), 4.17 (8 H, m), 5.31 (1 H, d, *J* 1.3), 5.48 (1 H, d, *J* 1.3); **14b** 0.87 (3 H, m), 1.03–1.48 (24 H, m), 2.99–3.21 (4 H, m), 4.17 (8 H, m) and 5.60 (1 H, t).

General Procedure for the Synthesis of Methylenecyclohexane Derivatives and Methylenecycloheptane Derivatives.—A mixture of Pd(dba)$_2$ (0.05 mmol), dppe (0.1 mmol) and THF (2 cm^3) was stirred until the solution became orange, then acetonitrile (4 cm^3) was added. Compound **15** or **21** (1 mmol) and prop-2-ynylic carbonates (1.3 mmol) were added. The mixture was heated at 80 °C until the reaction was complete. The products were isolated by flash column chromatography.

Tetraethyl 2-methylenecyclohexane-1,1,4,4-tetracarboxylate **16** (eluent: ethyl acetate–light petroleum, 1:10); δ_H(CDCl$_3$; 90 MHz) 1.25 (12 H, m), 1.80–2.40 (4 H, m), 2.88 (2 H, s), 4.20 (8 H, m), 4.86 (1 H, br s) and 5.09 (1 H, br s); ν_{max}(neat)/cm^{-1} 1733 (C=O) and 1644 (C=C); *m/z* 385 (M + 1)$^+$, 311 (base), 265, 237, 209, 119, 91 and 43 (Found: C, 59.5; H, 7.5. $C_{19}H_{28}O_8$ requires C, 59.36; H, 7.34%).

Tetraethyl 2-methylene-3-propylcyclohexane-1,1,4,4-tetracarboxylate **17a** and *tetraethyl 2-butylidenecyclohexane-1,1,4,4-tetracarboxylate* **17b** were isolated as a mixture (eluent: ethyl acetate–light petroleum, 1:15). The ratio was determined according to the olefin proton absorption in the ^{1}H NMR spectrum (1:3); ν_{max}(neat)/cm^{-1} 1732 (C=O) and 1444 (C=C); *m/z* 441 [(M + 1)$^+$], 368 (base), 293, 247, 145 and 91 (Found: C, 63.1; H, 8.35. $C_{23}H_{36}O_8$ requires C, 62.71; H, 8.24%); δ_H(CDCl$_3$; 300 MHz); **17a** 0.86 (3 H, m), 1.19–1.32 (18 H, m), 1.80–2.28 (5 H, m), 4.17 (8 H, m), 4.95 (1 H, s) and 5.17 (1 H, s); **17b**, 0.86 (3 H, m), 1.19–1.32 (18 H, m), 1.80–2.28 (4 H, m), 2.67–2.87 (2 H, m), 4.17 (8 H, m) and [5.15 (t), 5.43 (t), (1 H)].

Tetraethyl 3-butyl-2-methylenecyclohexane-1,1,4,4-tetracarboxylates **19a** and *tetraethyl 2-pentylidenecyclohexane-1,1,4,4-tetracarboxylate* **19b** (1:3, eluent: ethyl acetate–light petroleum, 1:15); ν_{max}(neat)/cm^{-1} 1730 (C=O) and 1444 (C=C); *m/z* 426 (M$^+$), 380, 353 (base), 307, 279 and 233 (Found: C, 61.9; H, 8.05. $C_{22}H_{34}O_8$ requires C, 61.95; H, 8.03%); δ_H(CDCl$_3$; 300 MHz) **19a** 0.86 (3 H, m), 1.22–1.42 (16 H, m), 2.03–2.33 (5 H, m), 4.21 (8 H, m), 4.98 (1 H, s) and 5.18 (1 H, s); **19b**, 0.86 (3 H, m), 1.22–1.42 (16 H, m), 2.03–2.33 (4 H, m), 2.70–2.80 (2 H, m), 4.21 (8 H, m) and [5.16 (t), 5.45 (t) (1 H)].

Tetraethyl 3-heptyl-2-methylenecyclohexane-1,1,4,4-tetracarboxylate **20a** and *tetraethyl 2-octylidenecyclohexane-1,4,4,4-tetracarboxylate* **20b** (1:2.3, eluent ethyl acetate–light petroleum, 1:15); ν_{max}(neat)/cm^{-1} 1733 (C=O) and 1444 (C=C); *m/z* 483 [(M + 1)$^+$], 409, 364, 289, 261 and 215 (Found: M$^+$, 482.2878. $C_{26}H_{42}O_8$ requires *M*, 482.2877); δ_H(CDCl$_3$; 300 MHz); **20a**, 0.87 (3 H, m), 1.22–1.36 (24 H, m), 2.02–2.31 (5 H, m), 4.20 (8 H, m), 4.97 (1 H, s) and 5.17 (1 H, s); **20b**, 0.87 (3 H, m), 1.22–1.36 (24 H, m), 2.02–2.31 (4 H, m), 2.69–2.89 (2 H, m), 4.20 (8 H, m and [5.15 (t), 5.42 (t), 1 H)].

Tetraethyl 2-methylenecycloheptane-1,1,4,4-tetracarboxylate **22** (eluent: ethyl acetate–light petroleum, 1:15); δ_H(CDCl$_3$; 300 MHz) 1.14 (12 H, t), 1.72–2.26 (6 H, m), 2.88 (2 H, s), 4.16 (8 H, m), 5.12 (1 H, s) and 5.21 (1 H, s); ν_{max}(neat)/cm^{-1} 1727 (C=O) and 1635 (C=C); *m/z* 399 [(M + 1)$^+$], 315, 297, 269, 251, 223, 201 and 173 (Found: C, 60.5; H, 7.7. $C_{20}H_{30}O_8$ requires C, 60.29; H, 7.59%).

Tetraethyl 2-butylidenecycloheptane-1,1,4,4-tetracarboxylate **23b**, δ_H(CDCl$_3$; 300 MHz) 0.87 (3 H, t), 1.15–1.38 (16 H, m), 1.70–2.27 (6 H, m), 2.98 (2 H, s), 4.16 (8 H, m) and 5.68 (1 H, t, 7.4); ν_{max}(neat)/cm^{-1} 1725 (C=O) and 1462 (C=C); *m/z* 440 (M$^+$), 367 (base), 337, 247, 173 and 145 (Found: C, 62.85; H, 8.75. $C_{23}H_{36}O_8$ requires C, 62.71; H, 8.24%).

References

1 Methylenecyclopentane derivatives (*a*) M. Franck-neumann, M. Miesch, E. Lacroxia and F. Barth, *Tetrahedron Lett.*, 1989, **30**, 3529; (*b*) C. Mohidol, C. Thebtaranonth, Y. Thebtaranonth and C. Yenjai, *Tetrahedron Lett.*, 1989, **30**, 3857, 3861; (*c*) M. A. Tins and S. Trehan, *J. Org. Chem.*, 1989, **54**, 46; Methylene cyclohexane derivatives; (*d*) R. C. Cambie, G. R. Clark and M. E. Geoth, *Aust. J. Chem.*, 1989, **42**, 497; (*e*) K. Sukurai, T. Kitahara and K. Mori, *Agric. Biol. Chem.*, 1989, **53**, 1449; (*f*) R. S. Harapanhalli, *J. Chem. Soc., Perkin Trans. 1*, 1988, 3149; Methylene cycloheptane derivatives (*g*) W. M. Daniewki, M. Gumulka and M. Budesinsky, *Collect. Czech. Chem. Commun.*, 1989, **54**, 1903, 1919; (*h*) S. Carmely, M. Cojocaru, L. Loya and Y. Kashman, *J. Org. Chem.*, 1988, **53**, 4801; (*i*) M. Ando, M. Kusaka, H. Ohara, K. Takase, H. Yamaoka and Y. Yanagi, *J. Org. Chem.*, 1989, **54**, 1952.

2 (*a*) L. A. Paquette, *Top. Curr. Chem.*, 1984, **119**, 1; (*b*) B. M. Trost, *Chem. Soc. Rev.*, 1982, 141; (*c*) T. Antonsson, C. Moberg and L. Totlie, *J. Org. Chem.*, 1989, **54**, 4914 and refs. cited therein.

3 (*a*) G. Stark and M. E. Reynelds, *J. Am. Chem. Soc.*, 1988, **110**, 6911; (*b*) B. M. Trost, D. C. Lee, *J. Am. Chem. Soc.*, 1988, **110**, 7255; (*c*) T. V. Rujanbabu, W. A. Nugeut, D. F. Taber and D. J. Fagan, *J. Am. Chem. Soc.*, 1988, **110**, 7128; (*d*) W. Oppolzer, J.-M. Gaudin and T. N. Berkinshaw, *Tetrahedron Lett.*, 1988, **29**, 4705; (*e*) W. Oppolzer, R. E. Swenson and J.-M. Gaudin, *Tetrahedron Lett.*, 1988, **29**, 5529; (*f*) B. Burns, R. Grigg, V. Sridharan and T. Worakun, *Tetrahedron Lett.*, 1988, **29**, 4325; 1988, **29**, 4329; (*g*) B. M. Trost, D. C. Lee and F. Rise, *Tetrahedron Lett.*, 1989, **30**, 651; (*h*) B. M. Trost and D. C. Lee, *J. Org. Chem.*, 1989, **54**, 2271.

4 B. M. Trost, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1.

5 C. Sahlberg and A. Claesson, *J. Org. Chem.*, 1984, **49**, 4120 and refs. cited therein.

6 (*a*) T. J. Luong and G. Linstunelle, *Tetrahedron Lett.*, 1980, **21**, 5019; (*b*) H. Westinijze, K. Ruitenberg, J. Meijer and P. Vermeer, *Tetrahedron Lett.*, 1981, **21**, 1771; (*c*) E. Keinan and E. Bosch, *J. Org. Chem.*, 1986, **51**, 4006.

7 T. Fujisawa, S. Iida and T. Sato, *Tetrahedron Lett.*, 1984, **25**, 4007.

8 E. Wenkert, M. H. Leftin and E. L. Michelotti, *J. Org. Chem.*, 1985, **50**, 1122.

9 (*a*) J. Tsuji, H. Watanabe, I. Minami and I. Shimizu, *J. Am. Chem. Soc.*, 1985, **107**, 2196; (*b*) I. Minami, M. Yuhara and J. Tsuji, *Tetrahedron Lett.*, 1987, **28**, 629; (*c*) I. Minami, M. Yuhara, H. Watanabe and J. Tsuji, *J. Organomet. Chem.*, 1987, **334**, 225.
10 L. Geng and X. Lu, *Tetrahedron Lett.*, 1990, **31**, 111.
11 For recent reviews on reactions of allylic compounds *via* (π-allyl)-palladium intermediates: (*a*) B. M. Trost, *J. Organometallic Chem.*, 1986, **300**, 263; (*b*) J. Tsuji, *J. Organomet. Chem.*, 1986, **300**, 281.
12 (*a*) B. M. Trost and M.-H. Hung, *J. Am. Chem. Soc.*, 1983, **105**, 7757; (*b*) B. M. Trost and M.-H. Hung, *J. Am. Chem. Soc.*, 1984, **106**, 6837; (*c*) B. M. Trost and M. Lautens, *Tetrahedron*, 1987, **43**, 4817.
13 (*a*) M. Scholz and H.-J. Kohler, *Tetrahedron*, 1969, **25**, 1863; (*b*) J. R. Dung, Y. S. Li and L. A. Carreira, *J. Chem. Phys.*, 1972, **57**, 1896.
14 B. M. Trost, T. N. Naminya and T. Satoh, *J. Am. Chem. Soc.*, 1985, **107**, 721.
15 J. Dale, *Stereochemistry and Conformational Analysis*, Universitetsforlaget, Verlag Chemie, New York, 1978, p. 174.
16 W. J. Bailey and W. R. Sorenso, *J. Am. Chem. Soc.*, 1956, **78**, 2287.
17 (*a*) N. Zelinsky, *Ber.*, 1989, **22**, 3294; (*b*) W. A. Noyes and L. D. Kryriakides, *J. Am. Chem. Soc.*, 1910, **32**, 1057; (*c*) V. P. Golinov, *Zh. Obshch. Khim.*, 1949, **19**, 1679.

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