Palladium-Mediated Cycloaddition Approach to Cyclopentanoids. Introduction and Initial Studies

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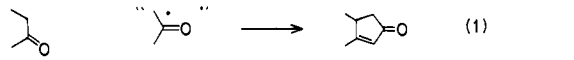
Abstract: (2-(Acetoxymethyl)-3-allyl)trimethylsilane, available from methallyl alcohol, serves as an equivalent of trimethylenemethane in cycloadditions to electron-deficient olefins. α,β-Unsaturated ketones, esters, nitriles, sulfones, and lactones serve as acceptors with this silane in the presence of a palladium(0) catalyst. Preformed $(Ph_3P)_4Pd$ or in situ reduction of palladium acetate or trifluoroacetate serves as such a catalyst. In addition to the acetate, the benzoate and methanesulfonate derivatives also participate. With *E* acceptors, high stereospecificity results; with *Z* acceptors, substantial crossover occurs. A two-step mechanism invoking a trimethylenemethane–palladium complex rationalizes the results.

The importance of cyclopentanoid natural products emerged in the decade of the sixties by the recognition of prostaglandins as monocyclic cyclopentane derivatives[1] and the identification of hirsutic acid as a polycondensed cyclopentane.[2] The rich diversity of structures that have been elucidated over the last decade heightens interest in methodology directed toward cyclopentane and its derivatives such as cyclopentenes, cyclopentanones, cyclopentenones, etc. Three-carbon annulations have taken a variety of forms. For example, reaction of an enolonium equivalent with a ketone followed by an aldol reaction (eq 1),[3] or a vinyl or-



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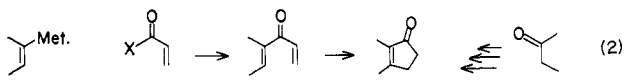
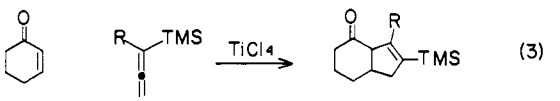


(2)

ganometallic, a vinylsilane, or olefin itself with an acrylic acid derivative[4] provides multistep approaches to cyclopentenones. The cyclopentenone shown in eq 2 is also available from ketones by using cyclopropyl[5] and propargyl alcohol[6] reagents.

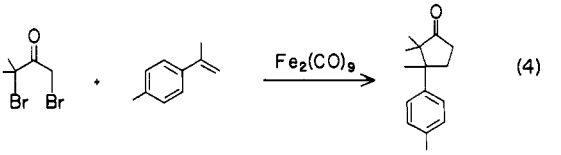
Cycloaddition-type methodology has the advantage of multibond formation occurring simultaneously or nearly so. Thus, structural complexity rapidly ensues.[7] The power of the Diels–Alder reaction in cyclohexane chemistry derives from this fact and the stereochemical consequences of such a concerted reaction. In fact, the tremendous success of the Diels–Alder reaction has led to its application to other ring sizes by subsequent ring enlargement or contraction sequences.[8] Jung developed an intriguing cycloaddition method based upon a Diels–Alder reaction relying on a two-carbon extrusion of the initial norbornyl adduct.[9]

Direct formation of a cyclopentyl ring by cycloaddition (excluding the 1,3-dipolar cycloaddition to five-membered-ring heterocycles) is rare. The reaction of propargyl chloride with olefins[10] or, more impressively, allenylsilanes (eq 3) with enones



(3)

in the presence of Lewis acids constitute recent entries.[11] Transition-metal-mediated reactions emerge for this purpose. Allyl–Fp conjunctive reagents combine with strongly electron-deficient olefins.[12] On the other hand, iron nonacarbonyl mediates the addition of polybromo ketones to electron-rich olefins (eq 4).[13,14] Zinc[15] and copper[16] also effect related condensations.



(4)

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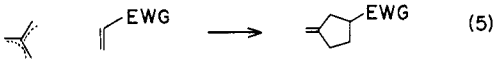
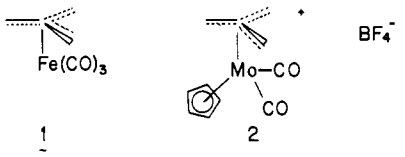
One of the most intriguing methods is the cycloaddition of trimethylenemethane to olefins,[17] which can be almost envisioned to be the Diels–Alder equivalent for five-membered rings (eq 5).



(5)

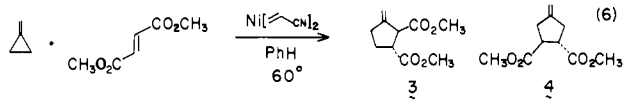
Except for very special systems, such a cycloaddition proceeds very poorly. An outstandingly successful application of this concept is the intramolecular version.[18]

Transition-metal complexes, among which are the iron (**1**)[19] and molybdenum (**2**)[20] complexes, have been prepared, but where



1 2

cycloadditions have been examined, results have been very disappointing. On the other hand, the cooligomerization of alkylidenecyclopropanes has achieved greater success. For example, bis(acrylonitrile)nickel catalyzes the cycloaddition of methylenecyclopropane with electron-deficient olefins (eq 6).[21,22] Pd(0)



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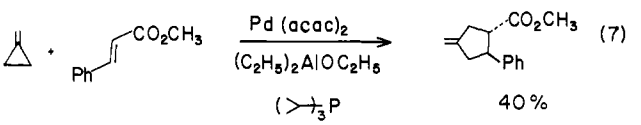
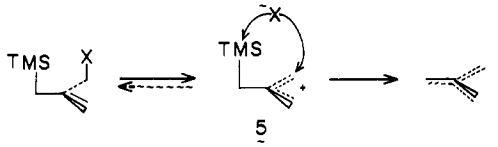


(7)

catalyzes similar reactions (eq 7).[23] The mechanism of such reactions remains unsettled. While trimethylenemethane metal complexes have been invoked for the palladium reaction, such a mechanism operates in only a few instances for the nickel reaction. For example, cycloadduct **4** does derive from such an intermediate; however, its companion **3** cannot. The latter substitution pattern appears to be the more general one with other acceptors.[22]

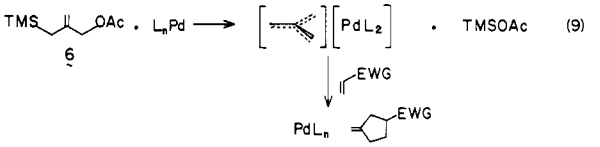
In searching for a mild method to generate trimethylenemethane (henceforth abbreviated TMM), we envisioned a method involving a species bearing both electrophilic and nucleophilic centers so

tuned that they do not instantly self-annihilate but that are capable of eliminating the elements of MX to give the desired trimethylenemethane. In this regard, the possibility that a silyl group could play such a role[24] depends upon the propensity that an intermediate such as **5** (eq 8) would have to desilylate compared



5 (8)

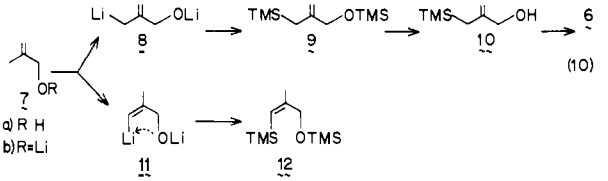
to simply neutralize charges. The ideal situation would make the latter reaction reversible. Given that oxygen anions are good silylophiles, X = OAc would prove desirable except for its poor ionizing ability. The ability of palladium(0) catalysts to promote the ionization of allylic acetates[25] suggested the reaction in eq 9,



6 (9)

which would generate not TMM itself but its palladium complex. If such a complex does indeed cycloadd to olefins, such a cycloaddition could be performed under very mild conditions in which the Pd would truly be a catalyst and the only byproduct would be trimethylsilyl acetate. The ready accessibility of the silyl acetate **6** from methallyl alcohol imparts further merit to this approach. In this paper and the accompanying paper, we wish to report the realization of this concept, the nature of the reactive intermediate, and the scope and limitations of the cycloaddition.[26]

Preparation of (2-(Acetoxymethyl)-3-allyl)trimethylsilane. Prior to this investigation, compound **6** and its feasible precursors were unknown in the literature. A simple synthesis is required in order to develop the chemistry of this bifunctional reagent. One possibility appeared to be the bis-silylation of α-methallyl alcohol dianion **8** to produce (2-((trimethylsiloxy)methyl)-3-allyl)trimethylsilane (**9**). Chemoselective hydrolysis of the silyl ether moiety of **9** should yield (2-(hydroxymethyl)-3-allyl)trimethylsilane (**10**). A straightforward acetylation would then furnish the necessary acetate **6** (eq 10).



(10)

The first step of the sequence proved difficult. Silylation of the dianion generated according to the method of Carlson[27a] (2 equiv of *t*-BuOK, 2 equiv of *n*-BuLi, hexane, 0 °C) with chlorotrimethylsilane gave very poor yields of **9** that was contaminated by other impurities. The procedure found to be relatively successful for this metalation was a modification of the one reported for dianion generation from 3-methyl-3-buten-1-ol using *n*-BuLi and TMEDA.[27b] However, the success of this approach is highly dependent on the reaction conditions. A critical variant appears to be the polarity of the reaction medium. When hexane was used as the solvent, in addition to the desired product **9**, substantial amounts (ca. 50%) of an isomeric vinylsilane were obtained. The identity of this side product, although not confirmed, was assumed to be 2-methyl-1-(trimethylsiloxy)-3-(trimethylsilyl)-2-propene (**12**). The assignment of the isomers is based on NMR spectroscopy. In the 100-MHz ^{1}H NMR spectrum of the mixture, **9** has two olefinic signals at δ 4.6 and 4.9, while **12** has only one

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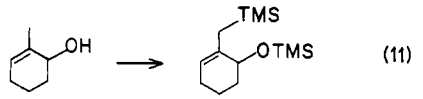
vinyl absorption at δ 5.3. In **9**, H_a is observed at δ 3.9; it is found downfield at δ 4.1 for **12**. The remaining allylic methylene protons of **9** resonate at δ 1.5 while **12** has an allylic methyl signal at δ 1.8. This observation led us to believe that in a nonpolar medium, complexation of the initially formed alkoxide **7b** with the active lithiating agent enhances the kinetic acidity of the syn vinyl proton on the methylene group. Such an internal activation is responsible for the formation of vinyl dianion **11** (which silylates to give **12**) instead of the thermodynamically more stable allyl dianion **8** required for the formation of desired product **9**.

If our postulation is correct, solvation of alkoxide **7b** by a more polar solvent should suppress the internal coordination and hence the amount of undesired dianion **11**. Indeed, if the bulk of the hexane in the *n*-BuLi solution was removed under reduced pressure and the metalation performed in pure ether, the amount of **12** was decreased to 15% and the overall yield of **9** was 60–70%. Using THF as the reaction medium gave a low conversion of starting material, but virtually only the desired product was observed. Unfortunately, THF is known to be decomposed by *n*-BuLi under prolonged treatment.[28] In dimethoxymethane or HMPA (1 equiv in ether), extremely poor yields were obtained; apparently these solvents are also unstable under the lithiating conditions. Interestingly, when an excess of TMEDA (without the removal of hexane) was used, a 1:1 ratio of **12** to **9** was observed. We decided to use a solvent mixture of THF and ether to take advantage of the selectivity in THF and the conversion in ether. After some experimentation, the best conditions appeared to be replacement of the hexane of the 2–2.5 equiv of *n*-BuLi by a 1.4:2.2 v/v ratio of THF:ether solution and 2 equiv of TMEDA. Initial alkoxide formation was performed at 0 °C and dianion generation at room temperature for 24–36 h. The red, insoluble, polymeric dianion was quenched at −10 to −30 °C with excess chlorotrimethylsilane. The yield of **9** after distillation was 50–65% and was only contaminated with less than 5% of **12**.

This method of allylsilane synthesis appears to be quite general. In the case of 2-methyl-2-cyclohexen-1-ol, where internal complexation cannot activate the vinyl proton, the dianion generation can be performed in pure hexane to give a 75% yield of the bis-silyl product (eq 11).[29]



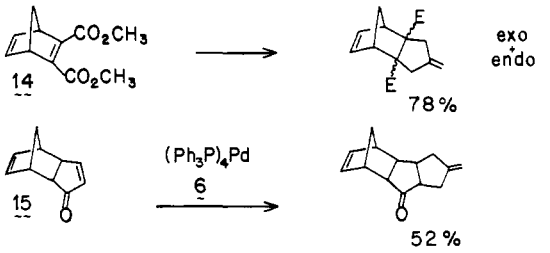
(11)

Compound **9** could be transformed directly to acetate **6** by the method of Ganem[30] using 10% $FeCl_3$ in acetic anhydride; however the yield was only 40%. The other alternative was to go through the allylic alcohol **10**. Although an allylic silane moiety is more stable to hydrolysis than a siloxy group, in dilute HCl, a 2:1 mixture of α-methallyl alcohol and the desired silane alcohol **10** was obtained, indicating substantial bis-desilylation. Changing the counterion from chloride (a potent silylophile) to the nonnucleophilic sulfate (i.e., using dilute H_2SO_4 instead of HCl) resulted in a quantitative yield of **10**.

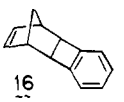
This procedure provides a convenient two-step route to the silane alcohol **10** by using inexpensive reagents. Since the discovery of this dianion approach, other routes to the same alcohol have also been developed. However, these methods often require more steps and the employment of relatively expensive (chloromethyl)trimethylsilane.[31,32]

Acetylation of **10** with acetyl chloride in pyridine and CH_2Cl_2 furnished the desired acetate **6** in 92% yield. Acetyl chloride is preferred over acetic anhydride because the rate is faster and the potentially silylophilic pyridinium hydrochloride precipitates out of the solution at 0 °C.

Cycloaddition Reaction. Bypassing the question of mechanism for the moment, the phenomenological question of whether cycloaddition to an olefin could occur was initially addressed by subjecting a mixture of an olefin and **6** to 3–9 mol % of $(Ph_3P)_4Pd$ (**13**). The ambident traps **14** and **15** chemoselectively led to



products derived from exclusive reaction at the electron-deficient double bond. Electronically rich olefins such as 1-morpholinostyrene, styrene, and furan or even strained electron-rich olefins like norbornene and the benzocyclobutene analogue **16** failed to react. Thus, the chemoselectivity exhibited by **14** and **15** derives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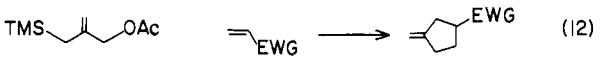
from the requirement for at least one electron-withdrawing group on the double bond as represented in eq 12 and summarized in Table I. For virtually all the examples of Table I, the reaction



(12)

conditions involved use of 3–9 mol % of **13** in the presence of 1–4 mol % of bis(diphenylphosphino)ethane (dppe) in hot toluene or refluxing THF. The fact that this is indeed a palladium-catalyzed reaction was demonstrated by a control experiment using methyl benzylidenemalonate (entry 12c). Only starting materials were isolated after 24 h of reflux in THF with 5 mol % PPh_3 but without $(Ph_3P)_4Pd$.

The stated isolated yields of the reaction are mostly based upon results obtained by using **6** as the limiting reagent since 2–3 equiv of the trap were normally employed. Synthetically, the acceptor would normally be the limiting reagent. In virtually every case in which recovery of the excess olefin was performed, the yield based upon consumed acceptor was higher (cf. entries 8, 13, 20, and 24). On this basis, the yields normally range from 50–98%. Such an excess of acceptor is unnecessary. For example, for entry 9 a 1:1 ratio of acceptor:**6** led to a 67% isolated yield of adduct.[33] In contradistinction to the Diels–Alder reaction, addition of a Lewis acid inhibited the reaction (entry 13c). The presence of the proposed byproduct, trimethylsilyl acetate, was confirmed by VPC comparison to an authentic sample in the case of entry 23a.

Adducts **17**, **19**, **22**, **23**, and **27** have spectral properties identical with those reported in the literature.[23] The methylenecyclopentane system present in the adducts is readily characterized by the olefinic multiplets at δ ~4.9–5.0 in the ^1H NMR spectrum. Furthermore, in the ^{13}C NMR spectrum, the quaternary and the methylene olefinic carbons resonate at δ 148–150 and 106–107, respectively. This is in good agreement with methylenecyclopentane itself (δ 152.9 and 104.3).[34] These are critical spectroscopic benchmarks for structural identification of the adducts obtained. Virtually all the products can be isolated by chromatography and are thermally stable (a number of adducts were routinely purified by preparative VPC). The exocyclic olefin moiety shows no tendency toward isomerization under the cycloaddition conditions.[35]

Addition of small amounts of dppe (0.6–0.8 equiv per equiv of $(Ph_3P)_4Pd$) prolongs the lifetime of the catalytic system and

(28) Jung, M. E.; Roberto, B. B. *Tetrahedron Lett.* **1977**, 3791.
(29) Trost, B. M.; Hiemstra, H. *J. Am. Chem. Soc.* **1982**, *104*, 886.
(30) Ganem, B.; Small, V. R., Jr. *J. Org. Chem.* **1974**, *39*, 3728.
(31) Hosomi, A.; Hashimoto, H.; Sakurai, H. *Tetrahedron Lett.* **1980**, 951.
(32) Knapp, S.; O'Connor, V.; Mobilis, D. *Tetrahedron Lett.* **1980**, 4557.
(33) Trost, B. M.; Renaut, P. *J. Am. Chem. Soc.* **1982**, *104*, 6668. Nanninga, T. N., unpublished work.
(34) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 71.
(35) In the palladium-catalyzed cooligomerization of methylenecyclopropane, double-bond migration has sometimes occurred. See ref 23.

Table I. Pd-Catalyzed Cycloaddition Reactions of 6[a]

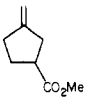
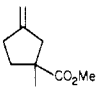
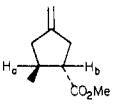
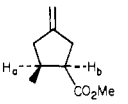
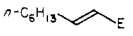
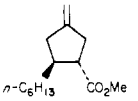
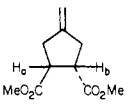
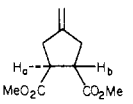
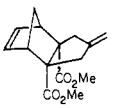
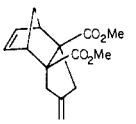
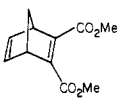
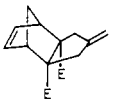
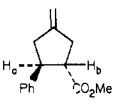
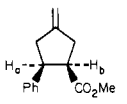
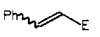
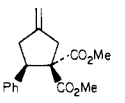
entry	trap/olefin	solvent	product			(yield)
			A. Ester (E = CO_2CH_3)			
1		$PhCH_3$	 17			(68)[f]
2		$PhCH_3$	 18			(50)[f]
			 19	 20		
3		$PhCH_3$	13.0	:	1	(30)[f,i]
4		(a) $PhCH_3$	1	:	1.7	(25)[f,i]
	E/Z = 1/7.5	(b) THF	1	:	1.6	(35)[f,i]
5		(a) $PhCH_3$				(23)[f]
		(b) THF				(51)[f]
			 21			
			 22	 23		
6		(a) $PhCH_3$	>99	:	<1	(10)[f,i]
		(b) THF	>99	:	<1	(32)[f,i]
7		(a) $PhCH_3$	25	:	1	(50)[f,i]
		(b) THF	1.3	:	1	(60)[f,i]
			 24	 25		
8	 14	(a) $PhCH_3$	4	:	1	(60)[f,j]
		(b) THF	4	:	1	(72,[f] 78[g])[j]
9	 14	(a) THF[m]	 26			(67)[f,g,n]
			 27	 28		
10		(a) $PhCH_3$[b]	95	:	5	(17)[f]
		(b) $PhCH_3$	95	:	5	(50)[f]
		(c) THF	95	:	5	(70)[f]
		(d) DMF[d]	95	:	5	(45)[f]
		(e) CH_3CN[d]	95	:	5	(11)[f]
		(f) PhH[e]	95	:	5	(48)[f]
11		(a) $PhCH_3$	1	:	2.0	(25)[f]
	E/Z = 1/10	(b) THF	1	:	1.3	(55)[f]
12		(a) $PhCH_3$[b]				(65)[f]
		(b) THF				(70)[f]
		(c) THF[c]	 19			starting material only

Table I (*Continued*)

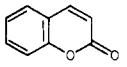
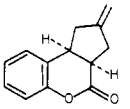
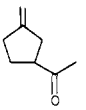
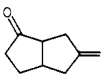
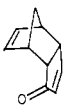
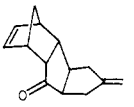
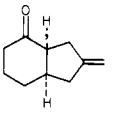
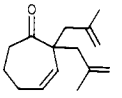
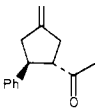
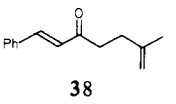
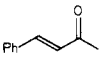
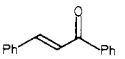
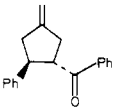
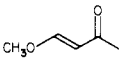
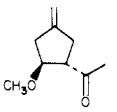
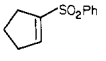
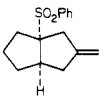
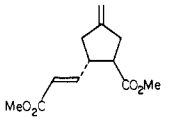
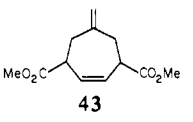
entry	trap/olefin	solvent	product	(yield)
		B. Lactone		
13		(a) $PhCH_3$ [b] (b) THF (c) THF	 30	(52) (56,[f] 85[g]) (13)[k]
		C. Nitrile		
14		$PhCH_3$ [b]	 31	(35)[f]
		D. Ketone		
15		$PhCH_3$ [b]	 32	(30)[f]
16		THF	 33	(56)[f]
17	 15	THF	 34	(52)[f]
18		THF	 35	(17)[f]
19		THF	 36	(18)[f]
			  37 38	
20		(a) $PhCH_3$ (b) THF	2.3 : 1 95 : 5	(45)[f] (45,[f] 82[g])
21		$PhCH_3$ [b]	 39	(85)[f]
22		THF	 40	(33)[f]
		E. Sulfone		
23		(a) $PhCH_3$ (b) THF	 41	(20)[f] (58)[f]

Table I (*Continued*)

entry	trap/olefin	solvent	product			(yield)
		F. Diene-Ester	 42		 43	
24		(a) THF	1.6	:	1	(47)[f]
		(b) dioxane	3.8	:	1	(58,[f] 98[g])

[a] Reactions are normally carried out with 1.5-3.6 equiv of olefin, 1 equiv of 6 (1-3 mmol), 3.8-8.8 mol % $(Ph_3P)_4Pd$, and 1.5-3.9 mol % dppe in refluxing THF or toluene at 80-110 °C. [b] For this run, no dppe was added. [c] Control experiment-$(Ph_3P)_4Pd$ replaced by 5 mol % of Ph_3P. [d] Room temperature. [e] Refluxing benzene (65 °C). [f] Isolated yield, based on silyl acetate 6 as limiting reagent. [g] Isolated yield, based on recovered olefin. [h] Ratio was determined by NMR spectroscopy at 100 MHz or 270 MHz with a 5% error limit. [i] Ratio was determined by VPC analysis with a 5% error limit. [j] Exo-endo ratio was determined by HPLC analysis with a 5% error limit. [k] 16 mol % of anhydrous $ZnCl_2$ was added to the reaction. [l] E = CO_2CH_3. [m] Catalyst formed in situ from $Pd(OAc)_2$ and $(i\text{-}C_3H_7O)_3P$. [n] Abstracted from ref 33.

prevents the deposition of palladium black. Although the rate of reaction is slightly reduced, the use of the external ligand improves the yield of the cycloaddition at least in one case (cf. entries 10a and 10b, where the yield increased from 17% to 50%). This observation is in accord with the results obtained in palladium-catalyzed alkylations of trisubstituted allylic systems.[25,36] At this point, the exact nature of the active catalyst is uncertain because of the equilibria between $(Ph_3P)_4Pd$ and dppe (eq 13).

$$(Ph_3P)_4Pd \underset{Ph_3P}{\overset{dppe}{\rightleftharpoons}} (dppe)(Ph_3P)_nPd \underset{Ph_3P}{\overset{dppe}{\rightleftharpoons}} (dppe)_2Pd \qquad (13)$$

The choice of solvent plays an important role in the cycloaddition. Changing from toluene to THF normally reduces the reaction time and enhances the yield (see entries 4-8, 10-13). In polar aprotic solvents such as acetonitrile and DMF, the reaction can even proceed at room temperature although the yields are somewhat lower (entries 10d and 10e). This dependence on solvent suggests the involvement of polar intermediates (vide infra). Benzene can also be used as a reaction medium (entry 10f).

The reaction exhibits moderate to high stereospecificity. From *E* olefins, virtually pure *E* adducts were obtained (entries 3, 5, 6, 10, 20, 21, 22, 24). On the other hand, *Z* olefins produced mixtures of *E* and *Z* methylenecyclopentanes (cf. entries 4, 7, 11). These isomeric mixtures were characterized by elemental analyses and/or NMR spectroscopy. Stereochemical assignments were supported by comparison to known compounds (for **19**, **22**, **23**, **27**)[23] as well as ^1H NMR spectroscopy. In *E*,*Z* pairs such as **19** and **20**, **27** and **28**, the *E* isomer exhibited the larger coupling constant between H_a and H_b (**19**, δH_a = 2.25, δH_b = 2.40, J_{ab} = 9 Hz; **27**, δH_a = 3.44, δH_b = 2.97, J_{ab} = 10.5 Hz) compared to the *Z* isomer (**20**, δH_b = 2.93, J_{ab} = 7.8 Hz; **28**, δH_a = 3.55, δH_b = 3.28, J_{ab} = 7.3 Hz). This data was extrapolated to the remaining cases to establish stereochemistry. In the ^1H NMR spectrum of **19** and **20** (adducts of methyl (*Z*)-crotonate), the methyl group resonates at δ 1.07 (d, J = 6.5 Hz) in the trans isomer **19** and at δ 0.89 (d, J = 7 Hz) in the corresponding cis isomer **20**. The olefinic and methoxy signals are at δ 4.84 and 3.69 for **19** and δ 4.89 and 3.67 for **20**. The ratio of **19** to **20** was determined by VPC (10% DC-710, T = 110 °C, R_t of **19** = 25 min, R_t of **20** = 31 min). For the adducts of methyl (*Z*)-cinnamate, the olefinic multiplet and methoxy singlet are at δ 4.93 and 3.55 for **27** and δ 5.00 and 3.34 for **28**. The ratio of isomers was determined by integration of the methoxy signals. The ^1H and ^{13}C NMR spectra of **22** and **23** (adducts of methyl maleate) are identical with the literature report.[23] The ratio was estimated by VPC (10% DC-710, T = 160 °C, R_t of **22** = 12 min, R_t of **23** = 14 min).

Table II. Cycloaddition Using Pd(II)/PPh_3 Catalytic System[a]

entry	olefin[f]	Pd(II)	PPh_3[c]	product (yield)[b]
1	A	$Pd(OAc)_2$		*d*, *e*
2	A	$Pd(OAc)_2$	4.3	**29** (73)
3	A	$Pd(OAc)_2$	2.0	**29** (28)
4	A	$Pd(O(CO)CF_3)_2$	3.8	**29** (12)
5	A	$(PPh_3)_2PdCl_2$	2.5	*d*
6	A	$(PhCN)_2PdCl_2$	4.2	*d*
7	B	$Pd(OAc)_2$	5.7	**27** (48)

[a] Reactions were carried out with ca. 2 equiv of olefin, 1 equiv of 6, 7-10 mol % Pd(II) salt, and 2-4 equiv of Ph_3P (based on Pd(II)) in refluxing THF. [b] Isolated yield (based on 6). [c] Mol % relative to the palladium(II) catalyst. [d] No cycloaddition, only starting materials were observed. [e] Palladium black was observed. [f] Olefin A = dimethyl benzylidenemalonate; olefin B = methyl (*E*)-cinnamate.

Partial loss of stereospecificity in the case of the *Z*-olefinic acceptors arises from isomerization of the acceptor itself under the reaction conditions. For example, when dimethyl maleate was used as the trap in toluene (entry 7a), the recovered starting material was found to be a mixture of maleate and fumarate (ca. 2.3:1). Similarly, methyl (*Z*)-cinnamate (entry 11a) equilibrated to a mixture of *E* and *Z* isomers in the ratio of 2:3. Thus, the moderate stereospecificity of the cycloaddition in these two cases may be explained by the scrambling of stereochemistry of the starting olefins. However, following the reaction of **6** with methyl (*Z*)-crotonate in THF by VPC (entry 4b) indicated that there was no isomerization of starting material during the course of the cycloaddition. Hence, at least in this case, the stereochemistry of the product reflects the mechanism of the cycloaddition.

Nature of the Catalyst. In all the entries of Table I save one, the catalyst was preformed $(Ph_3P)_4Pd$ (**13**).[37] One can also use palladium(II) salts with added Ph_3P as the catalytic system. The experimental procedure for such an approach is essentially identical with that of normal cycloaddition except for the nature of the catalyst. The results are summarized in Table II and experimental details in Table V. Although one starts with a Pd(II) salt, it seems that these are actually Pd(0)-catalyzed reactions because in the absence of the phosphine ligand, no cycloadduct was obtained and only palladium black was observed (entry 1). Furthermore, reduction of $Pd(OAc)_2$ to Pd(0) species by olefins is well-known.[38] Both palladium acetate and trifluoroacetate may be used although the former gave a more satisfactory yield. A $Pd(OAc)_2$-$(i\text{-}C_3H_7O)_3P$ catalyst has recently proven to be effective.[33] Soluble palladium chlorides did not give any product (entries 5, 6) because

(36) Trost, B. M.; Miller, M. J.; Schmuff, N. S. *J. Am. Chem. Soc.* **1980**, *102*, 5979.

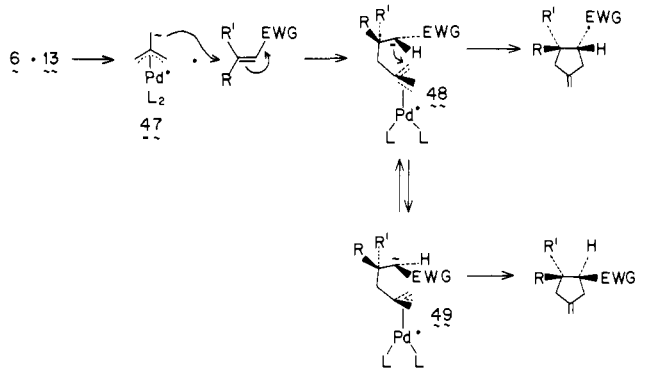
(37) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(38) Kitching, W.; Rappoport, Z.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1966**, *88*, 2054.

Table III. Dependence of Cycloaddition on Leaving Group

donor	X	cycloadduct 29 yield, %
6	OAc	70
44	O(CO)Ph	69
45	OSO_2CH_3	42
46	Br	

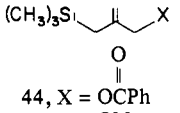
Scheme I. Mechanistic Proposal for Methylenecyclopentane Formation



the reduction to palladium(0) is more difficult. Tsuji also reported diene formation from allylic acetates when using a $Pd(OAc)_2/PPh_3$ system in which Pd(0) is claimed to be the active catalyst.[39] Similar to our observation, $(Ph_3P)_2PdCl_2$ failed to catalyze such a reaction.

There seems to be no significant differences in yields between the Pd(0) and Pd(II) approach. However, the latter does offer a unique advantage of being able to vary the nature of the ligand without having to prepare the corresponding palladium complex and avoids the need to handle air-sensitive complexes.

Nature of the Leaving Group. What allylic leaving groups can also serve as silylophiles? In addition to acetate, both benzoate **44** and mesylate **45**[40] gave respectable yields of adduct **29** when



44, X = OCPh
45, X = OMs
46, X = Br

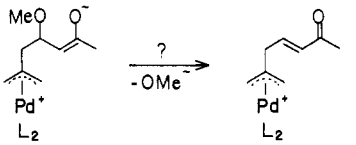
allowed to react with dimethyl benzylidenemalonate under typical conditions. However, allylic bromide **46** did not undergo cycloaddition. Table III summarizes the results.

Discussion

A general approach for the cycloaddition of the equivalent of trimethylenemethane to an electron-deficient olefin is in hand. The observations recorded herein make any concerted pathway such as a $\pi 4s + \pi 2s$ six-electron pathway adopted by a number of 1,3-dipolar cycloadditions[41] (e.g., reactions of olefins with nitrones and diazoalkanes) unlikely. We wish to propose that a TMM–Pd species such as **47** represents the reactive intermediate. This Michael donor initiates cycloaddition by conjugate addition to a Michael acceptor to generate a stabilized zwitterion **48**. While steric strain can be anticipated to accompany this 5-endo-trig ring-closure step, the accompanying charge neutralization provides a strong driving force. On the other hand, such steric constraints when magnified by the eclipsing interactions present with *Z*-olefinic acceptors increase the rate of bond rotation, i.e., **48** → **49**, at the expense of cyclization such that partial loss of stereospecificity occurs.

In light of this proposed mechanism, it is interesting that 4-methoxy-3-buten-2-one gave an adduct at all (entry 22). The cycloaddition probably proceeds through intermediate **50**, which apparently did not suffer β-elimination of methoxide anion spontaneously but rather ring closed to give the methylenecyclopentane product **40**.

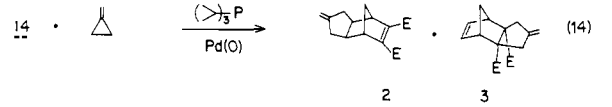
Not all electron-deficient olefins will undergo cycloaddition. Olefins such as 1,4-naphthoquinone, chloroacrylonitrile, and TCNE are too unstable to give adducts under the palladium-catalyzed conditions. Presumably, electron-transfer processes (e.g., oxidation of the Pd catalyst) in these cases disrupt the cycloaddition. On the other hand, methyl 3,3-dimethylacrylate (having two electron-donating alkyl groups on the β-carbon) also failed



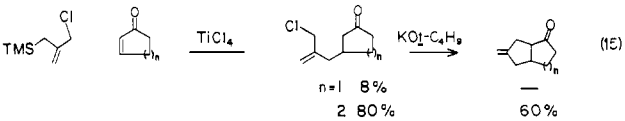
50

to give any methylenecyclopentane adduct because of its poor Michael acceptability. No trapping with isophorone was observed that may be due to a combination of both electronic deactivation and unfavorable steric interactions. So far, we have been unable to effect cycloaddition with acetylenes such as methyl phenylpropriolate and methyl tetrolate.

While such a mechanistic proposal not only rationalizes the observations to date and serves as a useful working hypothesis to predict new directions, conflicts with the cooligomerization of methylenecyclopropane exists.[23] For example, in the latter reaction norbornene serves as an acceptor to give the cycloadduct in 78% relative yield and the ambident acceptor **14** reacts at both double bonds (eq 14).[42] Clearly, two different pathways must be operative. Subsequent papers will consider this point in more detail. Synthetically, the two reactions vary in their efficiency in cycloadditions. For example, in the cooligomerization of methylenecyclopropane with methyl methacrylate, only a 6% yield of **18**[23] was obtained, and with cyclohexenone no cycloadduct at all.[43] As will be shown subsequently, substituted derivatives behave quite differently. The accessibility of methylenecyclopropane and the requirement for sealed vessels due to the high temperatures make the cooligomerization somewhat less convenient.



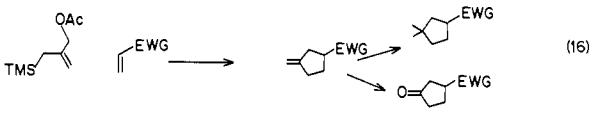
Bifunctional conjunctive reagents related to **6** can be induced to react with enones, especially those further activated, in a two-step sequence (eq 15).[32] In the case of cyclohexenone, this



method appears superior (48% vs. ~17%), but for cyclopentenone the one-step palladium-catalyzed cycloaddition is greatly superior. It also appears that the range of acceptors is more limited for this two-step sequence.

The methylenecyclopentane system generated by this efficient one-step approach is very useful. The very easy further conversion into a *gem*-dimethyl group, a common structural feature in many natural products, or a ketone, a versatile functional, group enhances the applicability of this methodology (eq 16).

(39) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett.* **1978**, 2075.
(40) Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1981**, *103*, 7380; *Tetrahedron Lett.* **1981**, *22*, 5023. Trost, B. M.; Vincent, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 5680.
(41) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *16*, 10.
(42) Binger, P., private communication.
(43) Balavoine, G.; Eshenazi, C.; Guillemot, M. *J. Chem. Soc., Chem. Commun.* **1979**, 1109.
(44) Trost, B. M.; Chan, D. M. T.; Nanninga, T. N. *Org. Synth.*, in press.



Experimental Section

General Methods. All anhydrous reactions were performed in flame-dried glassware under a positive pressure of dry nitrogen unless otherwise noted. Anhydrous solvents were transferred by flame-dried syringe. Solvents were distilled before use: hexamethylphosphoric triamide (HMPA), dimethyl sulfoxide (Me_2SO), dimethylformamide (DMF), acetonitrile (CH_CN), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), pyridine (C_5H_5N), hexane (C_6H_{14}), tetramethylethylenediamine (TMEDA), and pentane (C_5H_{12}) from calcium hydride; diethyl ether (Et_2O), tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), 1,4-dioxane, toluene ($PhCH_3$), and benzene (C_6H_6) from sodium benzophenone ketyl; methanol from magnesium; chlorotrimethylsilane from tributylamine. All palladium(0) catalysts were transferred under a nitrogen atmosphere in a glove bag. The term in vacuo refers to the removal of solvent on a Büchi–Brinkman Rotoevaporator at water-aspirator pressure; this is followed by evacuation of the flask (~0.1 mmHg) for 15–30 min [except for volatile compounds (bp <200 °C)]. Silica gel (Merck 60-PF 254) was used for analytical and all preparative (1.5 mm thick) thin-layer chromatography (TLC). The preparative TLC plates were activated at 120 °C for 2 h before use. Plastic-support precoated (Merck Silica gel 60 F_{254}, 0.2 mm) plates were also employed. Typical loadings on preparative plates were up to 80 mg on 20 × 10 cm, 80–200 mg on 20 × 20 cm, and 200–450 mg on 20 × 40 cm. Column chromatography was accomplished with Grace (grade 62, 60–200 mesh) silica gel. Removal of the material from silica gel was performed by extraction/washing with ethyl acetate or ether (for volatile products). High-pressure liquid chromatography (HPLC) was performed analytically on a Waters M6000 instrument with a porasil silica gel column (10 μm, Waters p/n 27477) unless stated otherwise. Preparative HPLC was performed on a Waters Prep 500 instrument with a self-packed, semiprep (2.5 × 30 cm, μPorasil, 37–75 μm, 50–400 mg) silica gel column or a Prepak-500 silica gel column (75 μm, 1–20 g). R_v refers to retention volume (CV = column volume). Flash chromatography was performed according to the method reported by Still.[45] Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. Gas chromatography was performed on a Varian Aerograph Model 90P (R = retention time). Column A refers to a 8 ft × $^3/_8$ in. column packed with 10% DC 710 on Chromosorb W. Column B refers to a 12 ft × 0.25 in. column packed with 15% Carbowax 20 M on Chromosorb W.

Proton NMR spectra were determined in chloroform-d (unless stated otherwise) on a Jeolco MH-100 (100 MHz) instrument or a Bruker WH-270 (270 MHz) spectrometer. Chemical shifts are reported in δ units, parts per million (ppm) downfield from tetramethylsilane (Me_4Si). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; br, broad. Coupling constants are reported in hertz (Hz). Infrared spectra (IR) were determined in the indicated solvent in 1-mm-thick solution cells on a Perkin-Elmer 267 or a Beckman Acculab 7 instrument and are reported in cm^{-1}. Carbon (^{13}C) NMR spectra were determined on a Jeolco FX-60 (15.4 MHz) or a Jeolco FX-200 (50.1 MHz) spectrometer. Chemical shifts are reported in δ units and splitting patterns are designated as with ^1H NMR. Deuterium (^2H) NMR spectra were determined on a Varian XL-100 (15.36 MHz) spectrometer. Chemical shifts are reported in δ units. Mass spectra were obtained on an AEI-902 instrument at an ionizing current of 98 mA and an ionizing voltage of 70 eV unless stated otherwise. Microanalyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI.

Preparation of (2-((Trimethylsiloxy)methyl)-3-allyl)trimethylsilane (9).[44] A 500-mL three-necked flask equipped with mechanical stirring, nitrogen inlet, and septum was charged with n-butyllithium (1.45 M in hexane, 170 mL, 246 mmol). The bulk of hexane was removed in vacuo by using a reduced-pressure pump or an aspirator at 15–30 mmHg. Anhydrous ether (135 mL) and TMEDA (40 mL, 264 mmol) were added at 0 °C. 2-Methyl-2-propen-1-ol (8.7 g, 121 mmol) was added dropwise over 15 min. THF (60 mL) was then introduced, and the reaction turned from cloudy to clear yellowish orange. The reaction was allowed to warm up to room temperature over 4–6 h and then was stirred for 32 h. To this dark red gummy mixture was added chlorotrimethylsilane (65 mL, 512 mmol) rapidly at 0 to −10 °C. The reaction mixture was stirred for 10 min and diluted with 1 L of ether. The dark cloudy mixture was washed with saturated sodium bicarbonate (250 mL), water (250 mL), saturated copper sulfate (2 × 250 mL), water (100 mL), and brine (200 mL) and dried over potassium carbonate. The solvent was removed in vacuo carefully, and the orange residue was then distilled via a Vigreux column to give 14.5 g (55%) of the title compound as a colorless oil (67 °C (5.5 mmHg)). An analytical sample was obtained by preparative VPC: R_t 10.5 min (column A, T = 100 °C, flow rate = 75 mL/min); ^1H NMR (270 MHz) δ 4.92 (m, 1 H), 4.63 (m, 1 H), 3.95 (br s, 2 H), 1.49 (br s, 2 H), 0.13 (s, 9 H), 0.03 (s, 9 H); IR (neat) 2943, 1641, 1245, 1081, 880, 836 cm^{-1}; mass spectrum, m/e (%) M^+ 216 (2), 148 (9), 147 (100), 113 (11), 75 (16), 73 (86), 54 (14). Calcd for $C_{10}H_{24}OSi_2$: 216.1358. Found: 216.1363.

A very minor (<5%) set of ^1H NMR signals was also observed: δ 5.3 (m), 4.1 (m), 1.8 (br s). These absorptions were attributed to the isomeric vinyl silane **12**.

Preparation of (2-(Hydroxymethyl)-3-allyl)trimethylsilane (10).[44] To a solution of **9** (13.5 g, 62 mmol) in 140 mL of THF was added 30 mL of 1 N H_2SO_4. The mixture was stirred rigorously for ca. 0.5 h at room temperature. Anhydrous potassium carbonate was added carefully until bubbling subsided. The reaction was diluted with 500 mL of ether, washed with saturated sodium bicarbonate (100 mL) and brine (100 mL), and dried over magnesium sulfate. The solvent was removed in vacuo with care to give 9.3 g (100%) of the alcohol **10** as a colorless oil. The crude material was carried on to the next step without purification. A sample was purified by preparative VPC: R_t 5.7 min (column A, T = 100 °C, flow rate = 75 mL/min); ^1H NMR (270 MHz) δ 4.91 (m, 1 H), 4.67 (m, 1 H), 3.98 (br s, 2 H), 1.55 (br s, 1 H), 1.54 (s, 2 H), 0.03 (s, 9 H); IR ($CHCl_3$) 3602, 3560–3340, 2950, 1638, 1247, 1038, 857 cm^{-1}; mass spectrum, m/e (%) M^+ 144 (14), 129 (53), 76 (20), 75 (100), 74 (18), 73 (93), 61 (18), 59 (11), 55 (12), 54 (88), 53 (16), 47 (13), 45 (60), 44 (91), 43 (36), 39 (65). Calcd for $C_6H_{16}OSi$: 144.0963. Found: 144.0962.

Preparation of (2-(Acetoxymethyl)-3-allyl)trimethylsilane (6). To a solution of **10** (7.7 g, 53 mmol) in pyridine (15 mL, 185 mmol) and 60 mL of methylene chloride at 0 °C was added acetyl chloride (6.5 mL, 91 mmol) dropwise over 10 min. The white cloudy mixture was stirred for 30 min and then diluted with 500 mL of ether. The mixture was washed with saturated sodium bicarbonate (2 × 100 mL), saturated copper sulfate (3 × 100 mL), water (100 mL), and brine (100 mL) and dried over anhydrous potassium carbonate. The solvent was removed by rotary evaporation and the residue distilled (95 °C (7 mmHg)) to give 9.1 g (92%) of the title compound as a colorless liquid: ^1H NMR (270 MHz) δ 4.88 (m, 1 H), 4.72 (br s, 1 H), 4.44 (br s, 2 H), 2.09 (s, 3 H), 1.55 (s, 2 H), 0.05 (s, 9 H); IR (neat) 3070, 2945, 2885, 1753, 1643, 1372, 1250, 1044, 840 cm^{-1}; ^{13}C NMR (15 MHz) δ 170.4, 141.7, 109.6, 67.84, 23.61, 20.86, −1.43; mass spectrum, m/e (%) M^+ 186 (5), 147 (13), 143 (18), 129 (11), 117 (34), 75 (40), 73 (100), 54 (42), 43 (18). Calcd for $C_9H_{18}O_2Si$: 186.1075. Found: 186.1075.

General Procedure for Palladium-Catalyzed Cycloaddition Reactions of 6. A 25-mL one-necked flask equipped with a magnetic stirring bar was charged with tetrakis(triphenylphosphine)palladium (4–9 mol %) under nitrogen in a glove bag. (2-(Acetoxymethyl)-3-allyl)trimethylsilane (6, 1–3 mmol), the acceptor (1.5–3.6 equiv), bis(diphenylphosphino)ethane [dppe (1.5–4 mol %) in some cases], and 4–8 mL (0.2–0.3 M in **6**) of solvent were added. The resulting mixture was heated to reflux or to the stated temperature under nitrogen immediately. The progress of the reaction was followed by TLC or VPC. After the reaction was completed, one of the following workup methods was used (Table IV). Method i—The reaction was filtered through a short column of silica gel and eluted with ether (100–150 mL). The eluent was concentrated in vacuo and the residue was purified by chromatography. Method ii—The reaction was concentrated under a stream of air and the residue was chromatographed. Method iii—The reaction mixture was chromatographed without any prior concentration or treatment of the solution. This workup procedure was often used to isolate volatile products.

Chromatography was performed on silica gel coated plates (see above for detail). The solvent reported for the R_f of the corresponding product was used for elution. Multiple elutions and/or more polar eluent were sometimes used, depending on the resolution. The product thus obtained was further purified by preparative VPC if necessary (especially for volatile products). A typical run is illustrated in the synthesis of *cis*-2-methylene-4,5-benzo-6-oxa-7-oxohydrindan (**30**).

Synthesis of *cis*-2-Methylene-4,5-benzo-6-oxa-7-oxohydrindan (30). A 25-mL flask was charged with **6** (183 mg, 0.98 mmol), tetrakis(triphenylphosphine)palladium (40 mg, 0.035 mmol), and dppe (6 mg, 0.015 mmol) under nitrogen in a glove bag. THF (4.5 mL) was added, followed by coumarin (296 mg, 2.03 mmol). The yellow solution was refluxed for 6.5 h. TLC indicated complete disappearance of **6**. The reaction was cooled to room temperature and concentrated under a stream of air. The residue was purified by preparative TLC (1:2 ether/pentane) to give 110 mg (56% based on **6**) of the title compound as

(45) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Table IV. Experimental Details for the Cycloadditions of 6

trap/olefin, entry; compound(s); equiv	6, weight, mg; mmol	$(Ph_3P)_4Pd$, weight, mg; mol %[b]	dppe, weight, mg; mol %[b]	solvent, volume, mL; temperature, °C; time, h	product, compound(s); weight, mg; yield,[g] %; workup method[a]
1; methyl acrylate; 4.5	434; 2.3	218; 8.5	none	toluene; 7; 87; 43	17; 210; 68; iii
2; methyl methacrylate; 3.3	520; 2.8	208; 6.8	34; 3.2	toluene; 7; 85; 67	18; 215;[d] 50; iii
3; methyl (*E*)-crotonate; 2.6	460; 2.4	120; 4.5	33; 3.6	toluene; 7; 110; 60	**19:20** (13:1);[e] 106;[d] 30; iii
4a; methyl crotonate;[h] 2.6	500; 2.8	134; 4.3	34; 3.2	toluene; 7; 110; 60	**19:20** (1:1.7);[e] 96;[d] 25; iii
4b; methyl crotonate;[h] 2.7	510; 2.8	114; 3.6	24; 2.2	THF; 7; reflux; 5.5	**19:20** (1:1.6);[e] 150;[d] 35; iii
5a; methyl (*E*)-2-nonenoate; 2.7	475; 2.6	165; 5.6	40; 3.9	toluene; 7; 100; 45	**21**; 130;[d] 23; i
5b; methyl (*E*)-2-nonenoate; 2.4	463; 2.5	90; 3.0	14; 1.4	THF; 7; reflux, 12	**21**; 282;[d] 51; ii
6a; dimethyl fumarate; 3.4	478; 2.5	200; 6.7	**34**; 3.5	toluene; 110; 140	**22**; 50;[d] ~10; i
6b; dimethyl fumarate; 2.7	365; 2.0	91; 4.0	12; 1.5	THF; 6; reflux; 285	**22**; 75;[d] 18; 32;[i] i
7a; dimethyl maleate; 3.6[j]	492; 2.6	140; 4.8	50; 5	toluene; 7; 100, 42	**22:23** (25:1);[e] i
7b; dimethyl maleate; 3.0[k]	474; 2.5	114; 4.0	12; 1.2	THF; 7; reflux; 210	**22:23** (1:1.3);[e] 310;[d] 60; i
8a; 14;[l] 3.1	467; 2.5	140; 4.8	10; 1.0	toluene; 7; 100; 23	**24:25** (4:1);[f] 400;[d] 60; i
8b; 14;[l] 2.1	381; 2.0	102; 4.3	15; 1.8	THF; 6; reflux; 36	**24:25** (4:1);[f] 390;[d] 72; 78;[c] i
9a; methyl (*E*)-cinnamate; 2.6	442; 2.3	91; 3.5	none	toluene; 7; 120; 43	**27:28** (95:5);[f] 83; 17; i
9b; same as 9a; 2.0	260; 1.4	53; 3.3	12; 2.1	THF; 4; reflux; 4.5	same as 9a; 212; 70; ii
9d; same as 9a; 2.0	264; 1.4	53; 3.3	11; 2.1	DMF; 4; ~30; 18	same as 9a; 120; 40[m]
9e; same as 9a; 2.1	300; 1.6	60; 3.2	10; 1.6	CH_3CN; 5.5; 30 °C for 96 h, 65 °C for 3 h	same as 9a; 40; 11; ii
9f; same as 9a; 2.3	326; 1.8	80; 4.0	12; 1.7	benzene; 6; 65; 19	same as 9a; 180; 48; ii
10a; methyl cinnamate;[n] 2.6	436; 2.3	12; 4.7	26; 2.9	toluene; 7; 110; 110	**27:28** (1:2);[f] 120;[d] 25; i
10b; methyl cinnamate;[n] 2.3	513; 2.8	200; 6.3	25; 2.3	THF; 7; reflux; 3	**27:28** (1:1.3);[f] 326;[d] 55; ii
11a; dimethyl benzylidene-malonate; 2.4	340; 1.8	180; 9	none	toluene; 7; 90; 5	**29**; 320; 65; i
11b; same as 11a	313; 1.7	143; 7.4	none	THF; 6; reflux; 1.5	**29**; 320; 70; ii
11c; same as 11a; 1.8	115; 0.6	none	Ph_3P; 62; 38	THF; 2.5; reflux; 45	none; only starting material
12a; coumarin; 2.3	420; 2.2	200; 8	none	toluene; 7; 116; 14	**30**; 220; 52; i
12b; run 1; coumarin; 2.1	183; 1.0	40; 3.5	6; 1.5	THF; 4.5; reflux; 6.5	**30**; 110; 56; ii
12b; run 2; coumarin; 0.5	350; 1.9	128; 4.5	9; 1.2	THF; 7; reflux; 10	**30**; 118; 67;[o] 85;[c] ii
12c;[p] coumarin; 1.5	220; 1.2	100; 7.3	9; 1.9	THF; 7; reflux; 48	**30**; 30; 13; ii
13; acrylonitrile; 13	480; 2.6	173; 5.8	none	toluene; 3.5; 60; 150	**31**; 100;[d] 35; i
14; methyl vinyl ketone; 4.5	385; 2.0	200; 8.8	none	toluene; 7; 80; 42	**32**; 70; 30; iii
15; cyclopentenone; 2–9	339; 1.8	100; 4.8	10; 1.4	THF; 7; reflux; 20	**33**; 137; 56; iii
16; 96; 2.2	315; 1.7	150; 7.7	10; 1.5	THF; 8; reflux; 42	**34**; 174; 52, 70;[c] ii
17; cyclohexenone; 3.6	470; 2.5	173; 6.0	22; 2.0	THF; 7; reflux; 20	**30**; 60;[d,q] 17; iii
18; cycloheptenone; 2.2	320; 1.7	94; 4.7	10; 1.5	THF; 9; reflux; 40	**36**; 33;[q] 18; iii
19a; benzylideneacetone; 2.4	463; 2.4	143; 5.2	33; 3.5	toluene; 7; 115; 35	**37:38** (2.3:1);[r] 200; 43; i
19b; benzylideneacetone; 2.3	350; 1.9	175; 8.0	20; 2.7	THF; 6; reflux; 5	**37:38** (95:5);[r] 163; 43; i
20; chalcone; 2.2	390; 2.1	183; 8.0	none	toluene; 7; 117; 11	39; 442; 85; i
21; 4-methoxy-3-buten-2-one; 3.8	380; 2.0	116; 4.9	24; 2.9	THF; 7; reflux; 3	40; 100; 33; iii
22a; 1-(phenylsulfonyl)-2-cyclopentene; 1.8	418; 2.2	153; 6.2	30; 3.6	toluene; 7; 110; 18	41; 110;[q,t] 20; i
22b; same as 22a; 1.3	443; 2.4	130; 4.7	14; 1.5	THF; 7; reflux; 40	41; 360; 58; ii
25a; dimethyl (*E,E*)-muconate; 1.3	237; 1.3	78; 5.3	13; 2.3	THF; reflux; 48	**43**; 52; 18; **42**; 80; 29; ii
25b; same as 25a; 1.4	223; 1.2	98; 7.1	10; 1.5	dioxane; 5; reflux; 8	**43**; 112; **42**; **43**; **42:43**; 58, 98[c]
generation of dimethyl benzylidenemalonate; 2.2	TMM-Pd from 44; 227; 0.9	85; 8	8; 1.5	THF; 5.5; reflux; 11	**29**; 171; 69; ii
same as above; 2.5	45; 210; 0.96	86; 8.0	7; 1.3	THF; 5; reflux; 40	**29**; 110; 42
same as above; 2.1	46; 360; 1.7	170; 8.6	10; 2.0	THF; 7; reflux; 48	only starting material

[a] Workup method, see general procedure for cycloaddition. [b] Mol % with respect to 6. [c] Yield based on recovered olefin/trap. [d] The product was contaminated by solvent or starting material. The amount of product present was estimated by ^1H NMR (100 MHz) analysis of the mixture. [e] Ratio determined by VPC (see text). [f] Ratio determined by NMR spectroscopy (see text). [g] Yield based on 6 unless stated otherwise. [h] Obtained by the hydrogenation of methyl tetrolate in methyl acetate with Lindlar catalyst. $E/Z = 1/1.75$ (determined by ^1H NMR spectroscopy). [i] Yield based on recovered 6. [j] The olefin was isomerized to $E/Z = 1/2.3$. [k] The olefin was isomerized to $E/Z = 1/10$. [l] The starting material was obtained by the Diels–Alder reaction of cyclopentadiene with dimethyl acetylenedicarboxylate. [m] A different workup procedure was adopted. The reaction was diluted with ether (80 mL), washed with water (3 × 30 mL), dried over magnesium sulfate, concentrated, and purified by preparative TLC. [n] The starting material was obtained by the hydrogenation of methyl phenylpropiolate in ethyl acetate with Lindlar catalyst. $E/Z = 1/10$ (determined by ^1H NMR spectroscopy). [o] Yield based on the olefin. [p] For this run, anhydrous $ZnCl_2$ (26 mg, 16 mol %) was added. [q] A number of uncharacterizable products was also observed. [r] The ratio was estimated by integration of olefinic signal at δ 4.9 (**37**) and δ 4.7 (**38**). The mixture was separated by preparative VPC. [s] Because of the extensive polymerization, the acrylonitrile was added in three portions. [t] About 350 mg of liquid was obtained by distillation (bp <100 °C) of the reaction mixture. VPC (column B) analysis of the liquid indicated it was a mixture of mostly toluene and a small amount of trimethylsilyl acetate (compared with an authentic sample).

a white solid: R_f 0.56 (1:2 ether/pentane); mp 53–55 °C; ^1H NMR (270 MHz) δ 7.27–7.02 (m, 4 H), 4.95 (m, 2 H), 3.43 (d of t, J = 9.5, 7.3 Hz, 1 H), 3.14 (d of d of d, J = 7.3, 4.0, 0.7 Hz, 1 H), 3.03 (br d, J = 17.5 Hz, 1 H), 2.85–2.65 (m, 2 H), 2.39 (d of d of m, J = 16, 9.5, 2.5 Hz, 1 H); ^{13}C NMR (15 MHz) δ 169.6, 150.8, 146.4, 128.4, 128.1, 124.4, 123.5, 116.8, 107.8, 42.75, 40.35, 39.95, 35.03; IR ($CHCl_3$) 1753, 1662, 1590, 1493, 890 cm^{-1}; mass spectrum, m/e (%) M^+ 200 (100), 172 (26), 171 (13), 157 (17), 131 (13.5), 117 (17), 115 (9), 91 (15). Calcd for $C_{13}H_{12}O_2$: 200.0837. Found: 200.0831.

Methyl 3-Methylenecyclopentane-1-carboxylate (**17**): TLC R_f 0.7 (1:5 ether/pentane); ^1H NMR (270 MHz) δ 4.87 (m, 2 H), 3.68 (s, 3 H), 2.84 (quintet, J = 8.4 Hz, 1 H), 2.60–2.22 (m, 4 H), 2.03 (m, 1 H), 1.88 (d of q, J = 12.5, 8.4 Hz, 1 H); ^{13}C NMR (15 MHz) δ 175.5 (s), 150.0 (s), 105.7 (t), 51.32 (q), 43.84 (br s), 36.18 (br t), 31.95 (br t), 29.78 (br t); IR ($CHCl_3$) 2950, 1738, 1440, 1170, 835 cm^{-1}; mass spectrum, m/e (%) M^+ 140 (5), 109 (7), 100 (11), 84 (63), 83 (10), 82 (12), 81

Table V. Experimental Details for Cycloaddition Using Pd(II)/PPh_3 as the Catalytic System[b]

olefin, entry; compound; equiv	6, weight, mg; mmol	Pd(II), compound; weight, mg; mol %[a]	PPh, added, weight, mg; mol %[a]	THF, volume, mL; time, h	product, compound, weight, mg; yield,[a] %
1; dimethyl benzylidenemalonate; 2.3	340; 1.8	$Pd(OAc)_2$; 35; 8.5	none	7; 24	only starting materials
2; same as 1; 2.0	270; 1.5	$Pd(OAc)_2$; 30; 9.3	150; 39	5.5; 5	**29**; 290; 73
3; same as 1; 2.2	206; 1.1	$Pd(OAc)_2$; 18; 7.2	42; 14.5	4; 18	**29**; 146; 48
4; same as 1; 2.3	233; 1.3	$Pd(O(CO)F_3)_2$; 38; 10	124; 37	4; 3	**29**; 40; 12
5; same as 1; 2.1	222; 1.2	$(PPh_3)_2PdCl_2$; 55; 6.6	52; 17	4; 48	only starting materials
6; same as 1; 2.1	230; 1.2	$(PhCN)_2PdCl_2$; 33; 7	94; 30	4; 48	only starting materials
7; methyl (*E*)-cinnamate; 1.9	250; 1.3	$Pd(OAc)_2$; 22; 7.3	148; 42	4; 3.5	**27**; 140; 48

[a] Relative to 6. [b] The conditions for the Pd(II)/PPh_3 cycloaddition were the same as the general procedure for palladium(0)-catalyzed cycloaddition except $(Ph_3)_4Pd$ and dppe were replaced by the Pd(II) salt and Ph_3P, respectively. All reactions were performed in refluxing THF.

(100), 80 (64), 79 (28), 75 (13), 72 (16), 55 (13), 53 (14). Calcd for $C_8H_{12}O_2$: 140.0837. Found: 140.0838.

The ^1H NMR (C_6D_6, 100 MHz) spectrum was identical with the one published by Noyori.[22] The NMR (^{13}C and ^1H) spectral data were also essentially identical with those reported by Binger[23] for the same compound.

Methyl 1-Methyl-3-methylenecyclopentane-1-carboxylate (18): TLC R_f 0.4 (1:3 ether/pentane); VPC R_t 10.5 min (column, A, T = 115 °C, flow rate = 55 mL/min); ^1H NMR (270 MHz) δ 4.87 (m, 2 H), 3.67 (s, 3 H), 2.81 (br d, J = 16.3 Hz, 1 H), 2.40 (m, 2 H), 2.17 (m, 2 H), 1.23 (s, 3 H); ^{13}C NMR (15 MHz) δ 177.8, 150.3, 106.4, 51.72, 49.15, 44.47, 36.86, 30.92, 23.55; IR ($CHCl_3$) 2953, 1735, 1665, 1436, 1175, 1115, 882 cm^{-1}; mass spectrum, m/e (%) M^+ 154 (0.4), 105 (20), 95 (75), 94 (22), 79 (23), 58 (52), 43 (100), 41 (12), 39 (15). Calcd for $C_9H_{14}O_3$: 154.0993. Found: 154.0993.

Methyl *trans*-2-Methyl-4-methylenecyclopentane-1-carboxylate (19): TLC R_f 0.55 (1:10 ether/pentane); VPC R_t 25 min (column, B, T = 110 °C, flow rate = 70 mL/min); ^1H NMR (270 MHz) δ 4.84 (m, 2 H), 3.69 (s, 3 H), 2.61 (m, 3 H), 2.40 (q, J = 9 Hz, 1 H), 2.25 (q of q, J = 9, 6.5 Hz, 1 H), 1.95 (m, 1 H), 1.07 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (15 MHz) δ 175.4, 149.4, 105.9, 51.67, 51.44, 41.38, 38.86, 36.98, 19.03; IR ($CHCl_3$) 2960, 1725, 1432, 1365, 1028, 882 cm^{-1}; mass spectrum, m/e (%) 154 (3), 139 (11), 123 (12), 109 (14), 95 (100), 94 (53), 81 (51), 80 (11), 79 (53), 77 (12), 67 (16), 55 (20), 53 (18), 44 (13), 43 (86). Calcd for $C_9H_{14}O_2$: 154.0993. Found: 154.0994.

This compound has also been reported recently by Binger.[23] The spectral data were identical.

Methyl *cis*-2-Methyl-4-methylenecyclopentane-1-carboxylate (20): TLC same R_f as **19**; VPC R_t 31 min (same conditions as those for **19**). This compound was characterized by ^1H NMR only (270 MHz): δ 4.89 (m, 2 H), 3.67 (s, 3 H), 2.93 (q, J = 7.8 Hz, 1 H), 2.78–1.90 (m, 5 H), 0.89 (d, J = 7 Hz, 3 H).

Methyl *trans*-2-*n*-Hexyl-4-methylenecyclopentane-1-carboxylate (21): TLC R_f 0.6 (1:10 ether/pentane); VPC R_t 10.5 min (column A, T = 180 °C, flow rate = 60 mL/min); ^1H NMR (270 MHz) δ 4.84 (m, 2 H), 3.69 (s, 3 H), 2.60 (m, 2 H), 2.45 (q, J = 9 Hz, 1 H), 2.26–2.12 (m, 1 H), 1.99–1.88 (m, 1 H), 1.52 (br m, 10 H), 0.88 (br t, J = 6.3 Hz, 3 H); ^{13}C NMR (15 MHz) δ 175.9, 149.5, 105.9, 51.50, 50.24, 44.01, 39.09, 37.04, 34.64, 31.84, 29.43, 27.89, 22.63, 14.06; IR ($CHCl_3$) 2930, 2850, 1735, 1615, 1440, 1370, 1170, 1025, 880 cm^{-1}; mass spectrum, m/e (%) 224 (10), 165 (59), 164 (57), 139 (89), 109 (25), 107 (91), 95 (51), 94 (87), 93 (58), 81 (83), 80 (37), 79 (100), 77 (38), 67 (29). Calcd for $C_{14}H_{24}O_2$: 224.1775. Found: 224.1775.

Methyl *trans*-2-(Methoxycarbonyl)-4-methylenecyclopentane-1-carboxylate (22): TLC R_f 0.6 (1:10 ether/pentane); VPC R_t 12 min (column A, T = 160 °C, flow rate = 60 mL/min); ^1H NMR (270 MHz) δ 4.91 (m, 2 H), 3.71 (s, 6 H), 3.19 (m, 2 H), 2.82–2.71 (m, 2 H), 2.61–2.49 (m, 2 H); ^{13}C NMR (15 MHz) δ 174.1, 147.2, 107.3, 51.95, 46.87, 36.29; IR ($CHCl_3$) 2950, 1735, 1440, 1270, 1170, 1010, 885 cm^{-1}; mass spectrum, m/e (%) 198 (2.5), 139 (13), 138 (46), 113 (100), 109 (20), 95 (98), 94 (48), 85 (36), 84 (20), 81 (80), 80 (21), 79 (88), 59 (17). Calcd for $C_{10}H_{14}O_2$: 198.0892. Found: 198.0892. The spectral data were identical with those reported by Binger for the same compound.[23]

Methyl *cis*-2-(Methoxycarbonyl)-4-methylenecyclopentane-1-carboxylate (23): TLC, same R_f as **22**; VPC R_t = 14 min (same conditions as those for **22**). This compound was characterized by ^1H NMR only (270 MHz): δ 4.93 (m, 2 H), 3.67 (s, 6 H), 3.17 (m, 2 H), 2.82–2.49 (m, 4 H). The spectral data were identical with those reported by Binger for the same compound.[23]

A mixture of **22** and **23** (1:1.3) gave satisfactory elemental analysis. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.41; H, 7.10.

Exo and Endo Cycloadducts of 14 (24 and 25). The cycloadducts **24** and **25** (4:1) were characterized as a mixture. The major product was assumed to be the exo isomer **24**. The spectral assignments were based on relative intensity: TLC R_f 0.3 (1:5 ether/pentane); HPLC **24**, R_v 2.40 CV, **25**, R_v = 2.07 CV (μ Porasil, 10% ethyl acetate in hexane, flow rate = 0.8 mL/min).

24: ^1H NMR (270 MHz) δ 6.27 (t, J = 1.5 Hz, 2 H), 4.82 (septet, J = 1.5 Hz, 2 H), 3.60 (s, 6 H), 3.23 (d of m, J = 18.6, 2 Hz, 2 H), 2.86 (quintet, J = 2 Hz, 2 H), 2.51 (d of m, J = 18.6, 1.5 Hz, 2 H), 2.05 (d, J = 9.6 Hz, 1H), 1.35 (d of t, J = 9.6, 1.5 Hz, 1 H); ^{13}C NMR (15 MHz) δ 174.5, 151.3, 137.0, 104.9, 65.50, 53.44, 51.32, 44.23, 43.72.

25: ^1H NMR (270 MHz) δ 6.16 (t, J = 1.5 Hz, 2 H), 4.55 (septet, J = 1.5 Hz, 2 H), 3.67 (s, 6 H), 3.12 (quintet, J = 2 Hz, 2 H), 3.01 (d of m, J = 18, 2 Hz, 2 H), 2.31 (br d, J = 9 Hz, 1 H), 2.26 (br d, J = 18 Hz, 2 H), 1.51 (br d, J = 9 Hz, 1 H); ^{13}C NMR (15 MHz) δ 175.5, 151.7, 137.4, 103.3, 66.07, 51.72, 49.68, 44.23, 41.67.

24:25: IR (neat) 3070, 2940, 1740, 1658, 1436, 1236, 1200, 1085, 900, 887 cm^{-1}; mass spectrum, m/e (%) M^+ 262 (1.3), 197 (23), 165 (73), 164 (16), 77 (12), 66 (100), 44 (32), 40 (33). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92; M_r, 262.1200. Found: C, 68.75; H, 7.02; M_r, 262.1206.

The ratio of **24** to **25** was determined by integration of olefinic signals at δ 6.27, 4.82 (**24**) and δ 6.16, 4.55 (**25**). This was confirmed by HPLC analysis.

Methyl *trans*-2-Phenyl-4-methylenecyclopentane-1-carboxylate (27): TLC R_f 0.28 (1:10 ether/pentane); VPC R_t 21 min (column A, T = 170 °C, flow rate = 85 mL/min); ^1H NMR (270 MHz) δ 7.10–7.30 (m, 5 H), 4.93 (m, 2 H), 3.55 (s, 3 H), 3.44 (t of d, J = 10.5, 8.0 Hz, 1 H), 2.97 (t of d, J = 10.5, 8 Hz, 1 H), 2.87–2.76 (m, 2 H), 2.68 (d of d of q, J = 16.5, 11.3, 2.6 Hz, 1 H); ^{13}C NMR (15 MHz) δ 174.8, 148.5, 142.5, 128.4, 127.0, 216.6, 106.5, 51.50, 49.50, 41.15, 37.32; IR ($CHCl_3$) 2940, 1738, 1663, 1600, 1438, 1270, 1170, 880 cm^{-1}; mass spectrum, m/e (%) M^+ 216 (2), 157 (29), 156 (100), 155 (9), 141 (15), 129 (19), 128 (10), 115 (16), 91 (24), 79 (15), 77 (16). Calcd for $C_{14}H_{16}O_2$: 216.1150. Found: 216.1150.

The corresponding cis isomer **28** was present in ca. 5% [the ratio was determined by integration of methoxy signals at δ 3.55 (**27**) and δ 3.34 (**28**)].

This compound has also been reported by Binger.[23] The spectral data were identical.

Methyl *cis*-2-Phenyl-4-methylenecyclopentane-1-carboxylate (28): TLC, same R_f as **27**. This compound was characterized by ^1H NMR only (270 MHz): δ 7.10–7.30 (m, 5 H), 5.00 (m, 1 H), 4.97 (m, 1 H), 3.55 (q, J = 7.3 Hz, 1 H), 3.34 (s, 3 H), 3.28 (q, J = 7.3 Hz, 1 H), 2.95–2.52 (m, 4 H).

A mixture of **27** and **28** (1:2) gave satisfactory elemental analysis. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.79; H, 7.52.

Methyl 1-(Methoxycarbonyl)-2-phenyl-4-methylenecyclopentane-1-carboxylate (29): TLC R_f 0.56 (1:2 ether/pentane); ^1H NMR (270 MHz) δ 7.22 (m, 5 H), 5.00 (m, 2 H), 4.06 (d of d, J = 8, 6.4 Hz, 1 H), 3.71 (s, 3 H), 3.42 (br d, J = 17 Hz, 1 H), 2.92 (d of d of q, J = 17, 8, 2.2 Hz, 1 H), 2.87–2.72 (m, 2 H); ^{13}C NMR (15 MHz) δ 171.8 (s), 169.7 (s), 147.5 (s), 140.4 (s), 128.1 (m), 127.9 (m), 126.9 (m), 107.0 (t), 65.21 (s), 52.53 (q), 51.78 (q), 49.84 (q). 39.95 (t), 38.64 (t); IR ($CHCl_3$) 3020, 2960, 1730, 1663, 1600, 1498, 1438, 1278, 1043, 889 cm^{-1}; mass spectrum, m/e (%) M^+ 274 (15), 214 (23), 162 (61), 161 (15), 155 (46), 131 (100), 103 (56), 102 (13), 77 (40). Calcd for $C_{16}H_{18}O_2$: 274.1205. Found: 274.1200.

3-Methylenecyclopentane-1-carbonitrile (31): TLC R_f 0.4 (1:5 ether/pentane); ^1H NMR (270 MHz) δ 4.96 (m, 2 H), 2.86 (quintet, J = 7.4 Hz, 1 H), 2.72 (d of br d, J = 16.5, 7.4 Hz, 1 H), 2.65–2.47 (m, 2 H), 2.35 (d of t of m, J = 16.5, 7.4, 2.3 Hz, 1 H), 2.12 (m, 1 H), 1.98

(d of q, J = 12.6, 7.4 Hz, 1 H); ^{13}C NMR (15 MHz) δ 147.1, 126.9, 107.8, 37.49, 31.32, 31.09, 28.41; IR ($CHCl_3$) 2940, 2230, 1665 ,1440, 885 cm^{-1}; mass spectrum, m/e (%) M$^+$ 107 (2), 82 (43), 81 (30), 72 (28), 69 (21), 68 (24), 67 (63), 55 (39), 54 (60), 43 (100), 39 (80). Calcd for C_7H_9N: 107.0735. Found: 107.0735.

1-Acetyl-3-methylenecyclopentane (32): TLC R_f 0.38 (1:10 ether/pentane); VPC R_t 17 min (column A, T = 95 °C, flow rate = 60 mL/min); ^{1}H NMR (100 MHz) δ 4.86 (m, 2 H), 2.96 (quintet, J = 8.3 Hz, 1 H), 2.55–2.23 (m, 2 H), 2.17 (s, 3 H), 1.98 (d of t of d, J = 12.5, 8.3, 4.7 Hz, 1 H), 1.80 (d of q, J = 12.5, 8.3 Hz, 1 H); ^{13}C NMR (15 MHz) δ 209.6 (s), 150.4 (s), 105.9 (t), 52.41 (br d), 35.15 (br t), 32.35 (br t), 29.15 (q), 28.58 (t); IR ($CHCl_3$) 3055, 2942, 1712, 1663, 1431, 1360, 878 cm^{-1}; mass spectrum, m/e (%) M$^+$ 124 (5), 109 (23), 86 (18), 84 (31), 81 (70), 79 (14), 53 (10), 55 (15), 43 (100). Calcd for $C_8H_{12}O$: 124.0888. Found: 124.0888.

***cis*-7-Methylenebicyclo[3.3.0]octan-2-one (33)**: TLC R_f 0.21 (1:5 ether/pentane); VPC R_t 9.3 min (column, A, T = 130 °C, flow rate = 75 mL/min); ^{1}H NMR (270 MHz) δ 4.85 (m, 2 H), 2.85 (m, 1 H), 2.61 (m, 3 H), 2.48 (m, 1 H), 2.28 (m, 2 H), 2.26 (m, 2 H), 1.67 (d of t of d, J = 13.6, 8.1, 5.5 Hz, 1 H); ^{13}C NMR (15 MHz) δ 221.5, 150.3, 106.8, 51.78, 40.64, 39.21, 37.38, 35.03, 26.23; IR (neat) 3080, 2950, 1740, 1660, 1435, 1130, 1098, 882 cm^{-1}; mass spectrum, m/e (%) (30 eV) M$^+$ 136 (22), 121 (5), 108 (38), 107 (5), 93 (9), 92 (26), 91 (8), 80 (21), 79 (49), 77 (13), 58 (10), 53 (5), 43 (100), 41 (7), 39 (7). Calcd for $C_9H_{12}O$: 136.0885. Found: 136.0883.

Adduct of 15 (34): TLC R_f 0.31 (1:10 ether/pentane); ^{1}H NMR (270 MHz) δ 6.22 (d of d, J = 5.5, 3.2 Hz, 1 H), 6.07 (d of d, J = 5.5, 3.2 Hz, 1 H), 4.78 (m, 1 H), 4.72 (m, 1 H), 3.20 (m, 1 H), 3.09 (m, 1 H), 2.92 (d of d, J = 9.0, 5.0 Hz, 1 H), 2.66–2.57 (m, 2 H), 2.41 (m, 2 H), 2.33 (br m, 2 H), 2.01 (br d of d, J = 15.2, 7.2 Hz, 1 H), 1.51 (d of AB of t, J = 8.4, 1.3 Hz, 1 H), 1.39 (br d of AB, J = 8.4 Hz, 1 H); IR (neat) 3065, 2963, 2938, 1731, 1658, 1438, 1350, 1175, 1130, 888 cm^{-1}; ^{13}C NMR (15 MHz) δ 222.4, 149.9, 135.6, 134.9, 105.4, 54.98, 54.70, 51.67, 47.61, 47.10, 42.07, 41.72, 34.85; mass spectrum, m/e (%) 135 (52), 134 (22), 105 (14), 91 (60), 79 (22), 78 (22), 77 (17), 67 (11), 66 (100), 65 (31), 55 (17), 53 (11), 51 (12), 41 (11), 40 (32), 39 (83), 38 (13). Calcd for $C_{14}H_{16}O$: 200.1197. Found: 200.1198.

***cis*-2-Methylenehexahydroindan-7-one (35)**: TLC R_f 0.7 (3:20 ether/pentane); VPC R_t 12.5 min (column A, T = 147 °C, flow rate = 70 mL/min); ^{1}H NMR (270 MHz) δ 4.92 (m, 2 H), 2.76 (m, 2 H), 2.57 (m, 1 H), 2.50–1.51 (m, 9 H); ^{13}C NMR (15 MHz) δ 212.4, 149.0, 106.9, 52.69, 42.52, 39.26, 38.12, 33.32, 26.69, 23.89. IR ($CHCl_3$) 3080, 2010, 2970, 1707, 1430, 1315, 1230, 1145, 887 cm^{-1}; mass spectrum, m/e (%) (40 eV) M$^+$ 159 (10), 107 (15), 105 (26), 91 (16), 83 (27), 81 (12), 80 (17), 79 (100), 78 (25), 77 (88), 55 (12), 53 (18), 52 (12), 51 (33). Calcd for $C_{10}H_{14}O$: 150.1037. Found: 150.1049.

2,2-Diisobutenyl-3-cyclohepten-1-one (36): TLC R_f 0.4 (1:10 ether/pentane); VPC R_t 19 min (column A, T = 150 °C, flow rate = 65 mL/min); ^{1}H NMR (270 MHz) δ 5.78 (d of t, J = 12.6 Hz, 1 H), 5.51 (d, J = 12 Hz, 1 H), 4.82 (m, 2 H), 4.70 (m, 2 H), 2.56 (m, 2 H), 2.51 (d of AB, J = 14 Hz, 2 H), 2.24 (d of AB, J = 14 Hz, 2 H), 2.19 (m, 2 H), 1.82 (quintet, J = 7 Hz, 2 H), 1.72 (s, 6 H); IR (CCl_4) 3080, 2940, 1700, 1645. 1453, 1380, 894 cm^{-1}; mass spectrum, m/e (%) M$^+$ 218 (13), 163 (30), 162 (20), 147 (27), 145 (29), 134 (22), 119 (53), 107 (39), 105 (49), 93 (61), 91 (90), 81 (28), 79 (100), 77 (50), 67 (42), 65 (20), 55 (93), 53 (25), 43 (32), 41 (95), 39 (61). Calcd for $C_{15}H_{22}O$: 218.1665. Found: 218.1671.

***trans*-3-Acetyl-4-phenyl-1-methylenecyclopentane (37)**: TLC R_f 0.3 (3:20 ether/pentane); VPC R_t 12.5 min (column A, T = 170 °C, flow rate = 80 mL/min); ^{1}H NMR (270 MHz) δ 7.33–7.16 (m, 5 H), 4.92 (m, 2 H), 3.32 (t of d, J = 10, 8 Hz, 1 H), 3.16 (t of d, J = 10, 8 Hz, 1 H), 2.83 (br d of d, J = 16, 8 Hz, 1 H), 2.76–2.45 (m, 3 H), 1.93 (s, 3 H); ^{1C} NMR (15 MHz) δ 209.2, 148.7, 143.0, 128.5, 127.0, 126.6, 106.4, 57.53, 48.67, 41.75, 36.26, 29.98; IR ($CHCl_3$) 3060, 2940, 1715, 1662, 1600, 1496, 1359, 1170, 882 cm^{-1}; mass spectrum, m/e (%) M$^+$ 200 (1.5), 132 (16), 89 (13), 83 (19), 82 (100), 75 (12), 73 (71), 59 (13), 58 (15), 57 (22), 55 (13), 54 (13), 43 (88). Calcd for $C_{14}H_{16}O$: 200.1208. Found: 200.1201.

(*E*)-1-Phenyl-1,6-heptadien-3-one (38): TLC, same R_f as **82**; VPC R_t 26 min (same conditions as for **37**); ^{1}H NMR (270 MHz) δ 7.6–7.3 (m, 6 H), 6.76 (d, J = 16 Hz, 1 H), 4.76 (br s, 1 H), 4.72 (br s, 1 H), 2.81 (t, J = 7.4 Hz, 2 H), 2.39 (br t, J = 7 Hz, 2 H), 2.39 (s, 3 H); IR (neat) 2990, 1787, 1750, 1600, 1448, 1095, 970, 890 cm^{-1}; mass spectrum, m/e (%) M$^+$ 200 (5), 132 (26), 131 (100), 109 (20), 104 (20), 103 (82), 91 (15), 77 (58), 69 (11), 43 (15), 41 (29). Calcd for $C_{14}H_{16}O$: 200.1197. Found: 200.1199.

This compound was separated from **37** by preparative VPC. The ratio of **37** to **38** was determined by integration of olefinic signals at δ 4.7 (**38**) and δ 4.9 (**37**).

***trans*-3-Benzoyl-4-phenyl-1-methylenecyclopentane (39)**: TLC R_f 0.64 (1:3 ether/pentane); mp 65–68 °C; ^{1}H NMR (270 MHz) δ 7.87 (m, 2 H), 7.50–7.14 (m, 8 H), 5.16 (br s, 1 H), 5.12 (br s, 1 H), 4.15 (q, J = 9.1 Hz, 1 H), 3.93 (q, J = 9.1 Hz, 1 H), 3.13–3.01 (m, 2 H), 2.91–2.76 (m, 2 H); ^{13}C NMR (15 MHz) δ 200.4 (s), 148.8 (s), 143.0 (s), 136.5 (s), 135.5 (m), 128.1 (m), 127.9 (m), 126.1 (m), 106.1 (t), 57.73 (m), 47.61 (m), 40.64 (br t), 37.95 (br t); IR ($CHCl_3$) 3020, 2960, 1681, 1601, 1498, 1453, 1020, 890 cm^{-1}; mass spectrum, m/e (%) M$^+$ 262 (69), 157 (20), 115 (11), 105 (100), 91 (17), 77 (44), 69 (10), 59 (10), 55 (10), 51 (14), 45 (11), 43 (14), 41 (13). Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.92; M_r, 262.1358. Found: C, 86.89; H, 6.87; M_r, 262.1362.

***trans*-3-Acetyl-4-methoxy-1-methylenecyclopentane (40)**: TLC R_f 0.6 (1:4 ether/pentane); VPC R_t 4.6 min (column, A, T = 145 °C, flow rate = 85 mL/min); ^{1}H NMR (270 MHz) δ 4.89 (m, 2 H), 3.94 (q, J = 6.3 Hz, 1 H), 3.33 (s, 3 H), 3.05 (t of d, J = 8.8, 6.3 Hz, 1 H), 2.74–2.44 (m, 3 H), 2.33 (m, 1 H), 2.23 (s, 3 H); ^{13}C NMR (15 MHz) δ 208.7, 146.4, 107.6, 83.10, 57.50, 57.04, 38.58, 33.38, 29.61; IR ($CHCl_3$) 2920, 2820, 1708, 1620, 1365, 1110, 885 cm^{-1}; mass spectrum, m/e (%) M$^+$ 154 (0.2), 122 (10), 108 (13), 94 (23), 93 (16), 81 (21), 79 (32), 69 (10), 68 (16), 67 (23), 55 (14), 53 (11), 43 (100), 41 (31). Calcd for $C_9H_{14}O_2$: 154.0993. Found: 154.0988.

***cis*-1-(Phenylsulfonyl)-3-methylenebicyclo[3.3.0]octane (41)**: TLC R_f 0.5 (1:1 ethyl acetate/hexane); mp 65–66 °C; ^{1}H NMR (270 MHz) δ 7.93 (m, 2 H), 7.64 (m, 1 H), 7.55 (m, 2 H), 4.76 (m, 2 H), 3.19 (m, 1 H), 3.12 (br d, J = 15.5 Hz, 1 H), 2.54 (d of d of m, J = 14.9, 9.3, 1 Hz, 1 H), 2.43 (m, 1 H), 2.12 (d, J = 15.5 Hz, 1 H), 2.03 (br d, J = 14.9 Hz, 1 H), 1.92 (d of d of d, J = 12.3, 8.4, 6.5 Hz, 1 H), 1.69–1.47 (m, 3 H), 1.35 (sextet, J = 6.7 Hz, 1 H); ^{13}C NMR (15 MHz) δ 148.3, 137.5, 133.4, 129.7, 128.8, 107.2, 78.24, 45.38, 43.15, 40.18, 37.09, 34.29, 25.72; IR ($CHCl_3$) 3070, 2950, 1672, 1452, 1301, 1142, 1087, 885, 755, 715, 690 cm^{-1}; mass spectrum, m/e (%) M$^+$ 121 (29), 120 (100), 93 (28), 92 (39), 91 (27), 79 (47), 77 (17). Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92. Found: C, 68.64; H, 6.95.

Methyl (*E*)-[2-(Methoxycarbonyl)-4-methylenecyclopent-1-yl]-propenoate (42): TLC R_f 0.13 (1:10 ether/pentane); ^{1}H NMR (270 MHz) δ 6.90 (d of d, J = 15.8, 8.1 Hz, 1 H), 5.88 (d of d, J = 15.8, 1.1 Hz, 1 H), 4.92 (m, 2 H), 3.73 (s, 3 H), 3.69 (s, 3 H), 3.02 (br quintet, J = 9.2 Hz, 1 H), 2.78–2.54 (m, 4 H), 2.28 (d of d of q, J = 16, 10.6, 2 Hz, 1 H); ^{13}C NMR (50 MHz, partial) δ 149.27, 121.32, 107.19, 51.83, 51.48, 49.43, 45.76, 38.66, 36.62; IR (neat) 3070, 2948, 2841, 1735, 1720, 1655, 1440, 1369, 1206, 1110, 1040, 1020, 985, 890 cm^{-1}; mass spectrum, m/e (%) M$^+$ 224 (2.2), 193 (13), 192 (53), 165 (15), 164 (87), 133 (27), 132 (36), 105 (100), 104 (18), 91 (14), 79 (19), 78 (11), 77 (16), 59 (17), 55 (16), 44 (11), 39 (14). Calcd for $C_{12}H_{16}O_4$: 224.1044. Found: 224.1048.

Methyl *cis*-4-(Methoxycarbonyl)-6-methylene-2-cycloheptene-1-carboxylate (43): TLC R_f 0.17 (1:10 ether/pentane); ^{1}H NMR (270 MHz) δ 6.10 (d, J = 2.4 Hz, 2 H), 4.89 (s, 2 H), 3.73 (s. 6 H), 3.16 (br d, J = 10.8 Hz, 2 H), 2.70 (d of d, J = 13.4, 2.0 Hz, 2 H), 2.24 (d of d, J = 13.4, 10.8 Hz, 1 H); ^{13}C NMR (50 MHz) δ 174.03 (s), 146.70 (s), 130.68 (d), 113.94 (t), 52.01 (q), 45.39 (d), 38.85 (t); IR (neat) 3960, 1748, 1650, 1446, 1206, 1180, 1035, 916, 732 cm^{-1}; mass spectrum, m/e (%) M$^+$ 224 (1.2), 192 (38), 165 (34), 164 (25), 151 (13), 133 (25), 132 (37), 105 (100), 104 (14), 91 (19), 79 (14), 77 (13), 59 (26). Calcd for $C_{12}H_{16}O_4$: 224.1044. Found: 224.1048.

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Registry No. 6, 72047-94-0; **7a**, 513-42-8; **9**, 83378-96-5; **10**, 81302-80-9; **12**, 84642-39-7; **13**, 14221-01-3; **14**, 947-57-9; **15**, 15584-54-0; **16**, 32686-81-0; **17**, 37575-80-7; **18**, 52086-83-6; **19**, 68284-22-0; **20**, 72047-96-2; **21**, 72047-97-3; **22**, 37575-81-8; **23**, 37589-17-6; **24**, 74976-75-3; **25**, 74976-74-2; **27**, 72047-98-4; **28**, 72047-99-5; **29**, 72048-00-1; **30**, 72048-01-2; **31**, 54829-97-9; **32**, 54829-98-0; **33**, 84642-40-0; **34**, 84642-41-1; **35**, 72048-02-3; **36**, 84642-42-2; **37**, 74976-82-2; **38**, 84642-43-3; **39**, 72048-03-4; **40**, 84642-44-4; **41**, 72048-04-5; **42**, 82823-81-2; **43**, 82823-82-3; **44**, 84642-45-5; **45**, 74532-54-0; **46**, 84642-46-6; methyl acrylate, 96-33-3; methyl methacrylate, 80-62-6; methyl (*E*)-crotonate, 623-43-8; methyl (*Z*)-crotonate, 4358-59-2; methyl (*E*)-2-nonenoate, 14952-06-8; dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6; methyl (*E*)-cinnamate, 1754-62-7; methyl (*Z*)-cinnamate, 19713-73-6; dimethyl benzylidenemalonate, 6626-84-2; coumarin, 91-64-5; acrylonitrile, 107-13-1; methyl vinyl ketone, 78-94-4; cyclopentenone, 930-30-3; cyclohexenone, 930-68-7; cycloheptenone, 1121-66-0; benzylideneacetone, 122-57-6; chalcone, 94-41-7; 4-methoxy-3-buten-2-one, 4652-27-1; 1-(phenylsulfonyl)-1-cyclopentene, 64740-90-5; dimethyl (*E*,*E*)-muconate, 1119-43-3; 2-norbornene, 498-66-8; styrene, 100-42-5; furan, 110-00-9; Pd, 7440-05-3.