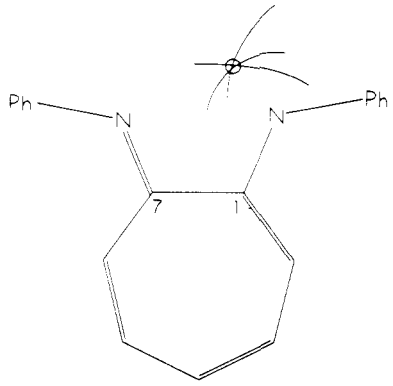

Figure 1. Position of the labile proton in 1-phenylamino-7-phenylimino-1,3,5-cycloheptatriene.

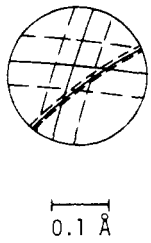

Figure 2. Inset from Figure 1 indicating propagated errors (- - -) in the computed loci (—).

The value of T_1^{DD} (H) for the ^{15}N nuclei correspond to internuclear N-H distance which precludes a symmetric structure for any reasonable C(1)-N-H bond angles. It is therefore necessary to determine loci of proton positions, relative to the probe nuclei, on the basis of rapidly equilibrating tautomers. It is not possible to do this explicitly, but the loci have been found by successive approximation and are depicted in Figures 1 and 2. It is the nature of the problem that a true skeletal geometry for the molecule is unavailable through diffraction methods. Nevertheless, a reasonable geometry can be predicted. That in Figure 1 is based on the X-ray structure of the dimethyl derivative except that averaged C(1)-N and C(7)-N bond lengths found in that structure have been increased and decreased, respectively, by 0.04 Å.[11] The N-C(ipso) bond lengths have been assumed to be 1.42 Å, the value found in *N,N'*-diphenyl-6-aminofulvene-2-aldimine.[13]

Figure 2 indicates the precision of the method, the outer pairs of loci (dashed lines) being based on the fully propagated errors in the calculations.[14] It is gratifying to note that there is a region of mutual intersection which defines the position of the proton. We believe that the greatest uncertainty is, in fact, that of the skeletal geometry. The N-H bond length, which is essentially independent of the skeletal geometry and is found with high precision (1.072 ± 0.004 Å) is a vibrationally averaged value. The C(1)-NH bond angle is 116 ± 3° in which, as can be seen from Figure 2, the uncertainty is associated primarily with the precision indices of the two loci calculated from the ^{13}C relaxation times. The position of the proton clearly establishes the presence of a symmetric double-well potential function for the hydrogen bond in this molecule. This agrees with observation[16] of a reasonably large (203-kHz) deuteron quadrupole coupling constant for the N-deuterated species. The proton is, in fact, located in the same position as a peak found near each nitrogen atom in a difference electron density synthesis described in the X-ray diffraction study.[9]

The procedure embodied in this example appears to be applicable to a number of related systems. In addition, it underscores the utility of ^{15}N as a sensitive probe for determining nitrogen-hydrogen internuclear distances.

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(14) The rotational diffusion parameters were calculated from the T_1 values for the 2(6), 3(5), 4, and para (para') carbon atoms by a nonlinear least-squares fitting of the equation $1/T_1 = \gamma_C^2\gamma_H^2\hbar^2 r_{CH}^{-6}(A\cos^2\Psi + B\sin^2\Psi)$ using a vibrationally averaged value of r_{CH} (1.107 Å[7]). This equation assumes the molecule can be treated as a planar uncoupled rotor.[15] The T_1 values were corrected for the small contributions of the "ortho" protons. The values of *A* and *B* so determined were then used to evaluate the unknown internuclear distances.
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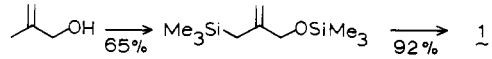
New Conjunctive Reagents. 2-Acetoxymethyl-3-allyltrimethylsilane for Methylenecyclopentane Annulations Catalyzed by Palladium(0)

Sir:

The increasing number of cyclopentanoid natural products and heightened interest in potentially anti-aromatic systems such as the pentalenes suggest the need for novel annulating approaches to cyclopentane systems.[1,2] We report herein that 2-acetoxymethyl-3-allyltrimethylsilane (**1**) serves as a novel annulating agent with olefins bearing electron-withdrawing groups in the presence of a palladium(0) catalyst[3] according to eq 1.

(1)

The requisite conjunctive reagent **1** was prepared by metalating α-methylallyl alcohol[4] (2 equiv of *n*-C_4H_9Li in ether,



2 equiv of TMEDA, 0 °C, then add THF, 0 °C → room temperature), followed by quenching with trimethylsilyl chloride.

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Table I. Methylenecyclopentane Annulations[a]

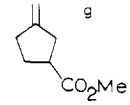
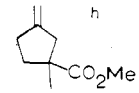
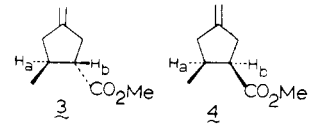
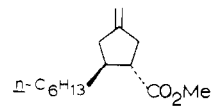
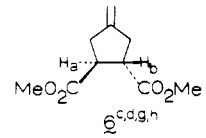
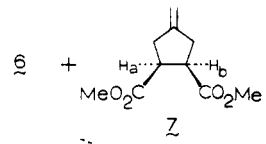
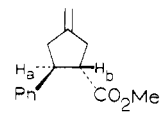
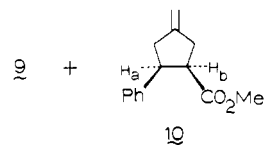
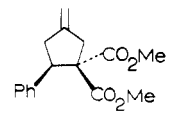
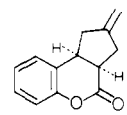
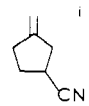
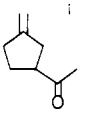
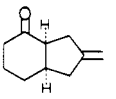
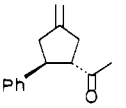
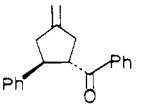
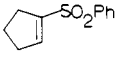
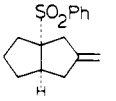
entry	olefin	solvent	temp, °C	time, h	product[f]	isold yield, %
			A. Esters			
1	methyl acrylate	$PhCH_3$[b]	85–90	43		68
2	methyl methacrylate	$PhCH_3$	85	67		50
						
3	methyl (*E*)-crotonate (**12**)	$PhCH_3$	110	60	**3:4**[c,d] 13:1	38
4	**12** + (*Z*)-methylcrotonate (**5**) **12:5** (1:7.5)	(a) $PhCH_3$	100	60	**3:4**[c,d] 1:1.7	25
		(b) THF	reflux	5.5	**3:4**[c,d] 1:1.6	35
5	methyl (*E*)-2-nonenoate	(a) $PhCH_3$	100	45		23
		(b) THF	reflux	12		51
6	dimethyl fumarate	(a) $PhCH_3$	105–110	140		10
		(b) THF	reflux	285		32
						
7	dimethyl maleate	(a) $PhCH_3$	100	42	**6:7**[d] 25:1	50
		(b) THF	reflux	210	**6:7**[d] 1.3:1	60
8	methyl (*E*)-cinnamate (**8**)	(a) $PhCH_3$[b]	115	43		17
		(b) $PhCH_3$	110	65		50
		(c) THF	reflux	4.5		70
						
9	**8** + methyl (*Z*)-cinnamate (**13**) **8:13** (1:10)	(a) $PhCH_3$	110	110	**9:10**[c] 1:2	25
		(b) THF	reflux	3	**9:10**[c] 1:1.3	55
10	methyl benzylidenemalonate	$PhCH_3$[b]	85–95	5		65
			B. Lactone			
11	coumarin	$PhCH_3$[b]	115	14		52
			C. Nitrile			
12	acrylonitrile	$PhCH_3$[b]	60	150		35

Table I (*Continued*)

entry	olefin	solvent	temp, °C	time, h	product[f]	isold yield, %
			D. Ketone			
13	methyl vinyl ketone	$PhCH_3$[b]	78	42		30
14	cyclohexenone	THF	reflux	20		17
15	benzylideneacetone	THF	reflux	5		43
16	chalcone	$PhCH_3$[b]	115	11	 [e]	85
			E. Sulfone			
17		(a) $PhCH_3$ (b) THF	110 reflux	18 40		20 58

[a] Reactions were normally carried out using 1.5–3.6 equiv of olefin, 1 equiv of **1**, 3.3–8.8 mol % $(Ph_3P)_4Pd$, and 1.5–3.9 mol % $Ph_3PCH_2CH_2PPh_2$ in the stated solvent at the stated temperature. Workup normally entailed direct evaporation and chromatography. [b] For this run, no $Ph_2PCH_2CH_2PPh_2$ was added. [c] *E:Z* ratio was determined by NMR spectroscopy at 270 MHz. [d] *E:Z* ratio was determined by VPC analysis. [e] In toluene, a 14% yield of 1-phenyl-6-methylhepta-1,6-dien-3-one was also obtained. [f] All products have been characterized by spectral data. New compounds also have satisfactory elemental composition. [g] Reference 5. [h] Reference 6. [i] Reference 7.

Hydrolysis (in H_2SO_4, THF, room temperature) and acetylation (AcCl, C_5H_5N, CH_2Cl_2, 0 °C) gave the desired reagent, bp 95 °C (7 Torr), in 60% overall yield from α-methylallyl alcohol.

For the cycloaddition, a mixture of the olefin, **1**, 3–9 mol % tetrakis(triphenylphosphine)palladium, and 1–4 mol % diphos was heated in toluene or refluxed in THF. As illustrated in Table I, a wide range of olefins gave the desired cycloaddition normally in 50–85% yields. All olefins that reacted bore an electron-withdrawing group including ester, nitrile, ketone, and sulfone. Simple alkyl substituted olefins like norbornene derivatives or electron-rich olefins like enamines failed to react. Tetracyanoethylene and methyl phenylpropiolate did not give adducts.

The choice of solvent plays a very important role. Switching from toluene to THF greatly shortened the reaction time and enhanced the yield of cycloaddition (see entries 5–9, 17). Generally, the addition of small amounts of diphos improved the reaction (cf. entry 8a to 8b where the yield increased from 17 to 50%).

From *E* olefins, virtually pure *E* products were obtained (entries 3, 5, 6, 8, 15, 16). On the other hand, *Z* olefins gave substantial crossover (entries 4, 7, 9). Following the reaction of methyl (*Z*)-crotonate by VPC[8] in THF suggested that the starting material retained its stereochemical integrity during the course of reaction, whereas dimethyl maleate isomerized under the cycloaddition conditions in $PhCH_3$. Thus, at least in the latter case, loss of stereochemistry stemmed in part from isomerization of the starting material.

Structural assignments were supported by comparison with known samples and spectral analyses. Spectral data is presented in the appendix (see paragraph at the end of the paper regarding supplementary material). In *E,Z* pairs, i.e., **3** and **4**, **9** and **10**, the *E* isomers exhibited the larger coupling constant between H_a and H_b (**3**, J_{ab} = 9 Hz; **9**, J_{ab} = 10.5 Hz) compared with the *Z* isomers (**4**, J_{ab} = 7.8 Hz; **10**, J_{ab} = 7.3 Hz). This data was used in the remaining cases to establish stereochemistry.

This reaction represents the equivalent of the addition of trimethylenemethane to olefins. In this regard, it is noteworthy that even cyclohexenone undergoes addition, albeit in modest yield. It is tempting to compare this reaction with the cycloaddition of trimethylenemethane[9] and its metal complexes[5-7,10-12] to olefins. In virtually all cases, the parent system adds in such low yields (5–20%) and only to such a limited range of olefins to make the reactions synthetically unattractive.[9a] The nickel catalyzed additions of methylenecyclopropane are most interesting in this regard.[5,7,10] Whereas reaction with methyl acrylate is reported[7] in 82% yield (not via the trimethylenemethane complex![5]), reaction with methyl methacrylate is reported[6] in 6% yield.

This simple one-step approach to cyclopentane annulation should be very useful synthetically. The exocyclic methylene group can serve as a protected carbonyl group as well as be useful for further elaboration. For example, cyclopropanation, followed by hydrogenolysis, can lead to a *gem*-dimethyl group as found in coriolins.[13] Synthetic applications of this new type of annulating reagent are under investigation. Mechanistic implications of this novel reaction are discussed in the accompanying manuscript.

Acknowledgment. We thank the National Science Foundation for their most generous support of our programs. We are grateful to Englehardt Industries and Mathey-Bishop for generous samples of palladium salts.

Supplementary Material Available: An appendix which includes NMR and/or IR spectra of compounds **1**, **3**, **4**, **9–11**, methyl (*E*)-2-*n*-hexyl-4-methylenecyclopentylcarboxylate, *cis*-2-methylene-7-oxohydrindan, *trans*-3-benzoyl-4-phenylmethylenecyclopentane, coumarin adduct (10-methylene-(*Z*)-cyclopent[*c*]chroman-2-one), and 1-benzenesulfonyl-3-methylenebicyclo[3.3.0]octane (2 pages). Ordering information is given on any current masthead page.

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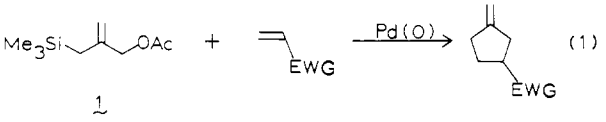
2-Acetoxymethyl-3-allyltrimethylsilane and Palladium(0): A Source of Trimethylenemethane-Palladium Complex?

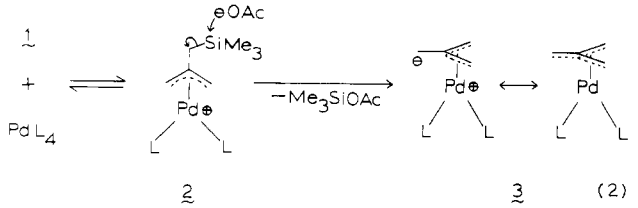
Sir:

In the previous paper,[1] we reported the cycloaddition of 2-acetoxymethyl-3-allyltrimethylsilane to electron-deficient olefins catalyzed by palladium(0) with formation of methylenecyclopentanes (eq 1). This rather surprising cycloaddition



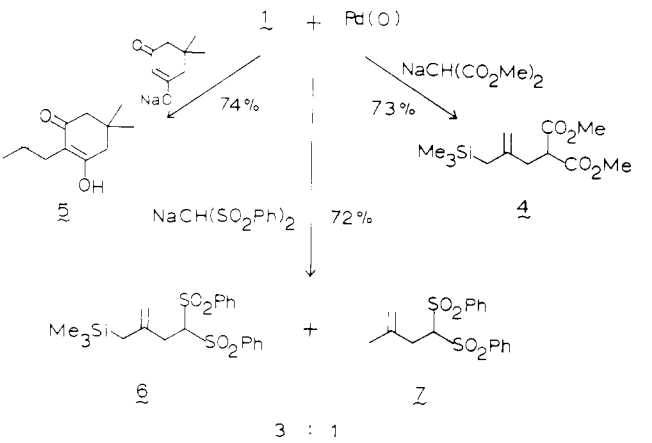
(1)

led us to propose the pathway in eq 2 as a working hypothesis. In this paper, we present evidence in support of this hypothesis—thus suggesting that **1** may be a valuable precursor to trimethylenemethane-metal complexes![2,3]



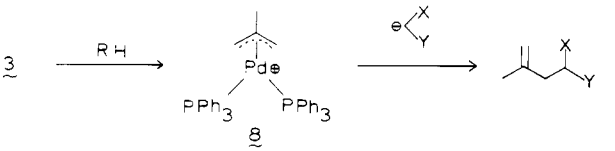
(2)

The initial formation of **2** is suggested by the reaction of **1** with dimethyl sodiomalonate to give the alkylated product **4.**[4] On the other hand, reaction with the anion of dimedone gave only the product of alkylation and desilylation, **5.** Interestingly, the anion of bis(benzenesulfonyl)methane leads to a mixture of **6** and **7.**



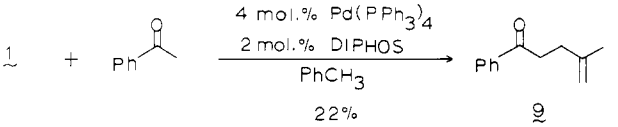
3 : 1

The formation of desilylated products does not arise from protodesilylation of the product or **1** under the reaction conditions as demonstrated by control experiments. Thus, some intermediate must be undergoing desilylation to lead to **5** and **7.** Apparently, if a nucleophile is kinetically slow in attacking **2, 2** lives long enough to suffer desilylation and generation of **3.** The latter is protonated by the excess dimedone or bis(benzenesulfonyl)methane or their alkylated products to give **8** which then reacts with starting nucleophile to give the desi-



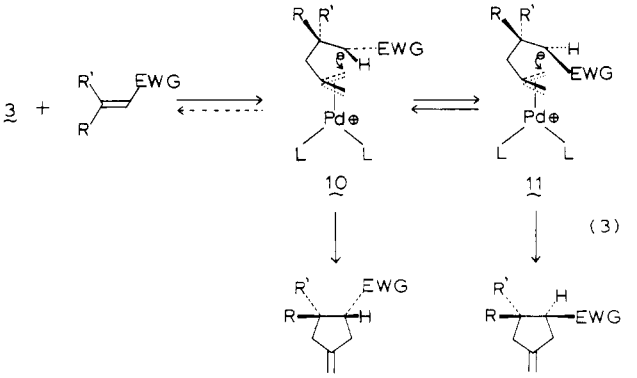
lylated product. Thus, the order of reactivity of the three nucleophiles toward **2** is malonate > bis(benzenesulfonyl)methane anion > dimedone anion—accounting for the straight alkylation with malonate, a competition of alkylation and desilylation with the sulfone system, and complete desilylation with dimedone.

To test this idea, **1** was reacted with acetophenone in the presence of the Pd(0) catalyst. Ketones do not react with allylic acetates in the presence of catalyst without a base.[4] The fact that desilylated-alkylated product **9** was obtained indicates



that a base formed to generate the enolate of acetophenone and **8.**[5] This observation strongly implicates **3** as that base.

That the cycloaddition intermediate is a nucleophile and not an electrophile is indicated by its reaction with electron-deficient olefins and its failure to react with electron-rich ones. The reaction can be rationalized as shown in eq 3.[6] The partial loss of stereochemistry, i.e., methyl (*Z*)-cinnamate (*Z*:*E*, 10:1) gives a 1:1.3 ratio of *E* and *Z* isomers of methyl 2-phenyl-4-methylenecyclopentylcarboxylate, indicates equilibration of



(3)

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