of gaseous methanethiol produced an insoluble ammonium salt. Freshly cut sodium or potassium metal, added in small pieces, reacted quickly. It was convenient to alternate the addition of thiol and metal to give a clear solution. The concentration of sodium thiomethoxide was calculated from the amount of metal consumed. Addition of a small excess of metal turned the solution blue, indicating the complete conversion of thiol. A small crystal of ferric nitrate hydrate catalyst then was added along with the appropriate quantity of metal to make amide ion. The formation of amide in the presence of thiolate ion appears to be unusually slow, requiring hours.

Substrate was added, occasionally dissolved in ether, and a deep color appeared. After the mixture was refluxed, excess NH_4Cl was added and the deep color faded immediately. Solvent was allowed to evaporate following the addition of 50 mL of ether. The resulting solid then was dissolved in water and extracted with three portions of ether and dried (sodium sulfate). Prior to analysis of the concentrated ether extracts by NMR, *tert*-butyl alcohol was added as an internal standard. Some yields were calculated from NMR data, the area of H-3 generally serving as a measure of the isoquinoline. All yield data given in Table I that use NMR as a method of analysis are based on a weighed amount of substrate as the limiting reagent. Evaporation of the ether gave product, purified by standard methods. Mixtures were not always separated, however.

Sodium anilide was generated by the addition of a known amount aniline to the thiomethoxide–amide ion mixture prior to the addition of substrate.

Reactions requiring the removal of samples were carried out in a 50-mL three-necked flask having a stopcock attached near the bottom. Mesitylene was added to the 50-mL flask to serve as an NMR standard. Samples of the ammonia mixture were run through the stopcock into 3 × 30 cm test tubes containing ammonium chloride and cooled in a flask of acetone–dry ice. Stirring these aliquots caused the deep color to bleach. Ether then was added, the solvent was allowed to evaporate prior to analysis by NMR. A control reaction consisting of the usual contents but not amide ion showed that the mole ratio of 4-bromoisoquinoline to mesitylene determined by NMR on a recovered sample agreed to within 10% of that calculated from the weights of materials used in the ammonia mixture. The method of recovery appears to be suitably quantitative.

Unsuccessful attempts were made to observe by proton NMR reactions in liquid ammonia. A sample consisting of 0.7 M 1, 1.4 M $NaSCH_3$, and 1.4 M $NaNH_2$ was very viscous and dark brown. Spectra taken at −40 and 0 °C were poorly resolved.

The reaction flask was cooled in an acetone–dry ice bath prior to the addition of substrate for reactions at −65 °C.

Residues of reaction mixtures were spotted on silica gel plates (GF_{254}, Merck) and developed with various solvents by vertical ascension in a closed tank.

All reactions were conducted under an atmosphere of air.

Synthesis of 1,4-Keto Esters and 1,4-Diketones via Palladium-Catalyzed Acylation of Siloxycyclopropanes. Synthetic and Mechanistic Studies

Tsutomu Fujimura, Satoshi Aoki, and Eiichi Nakamura*,†

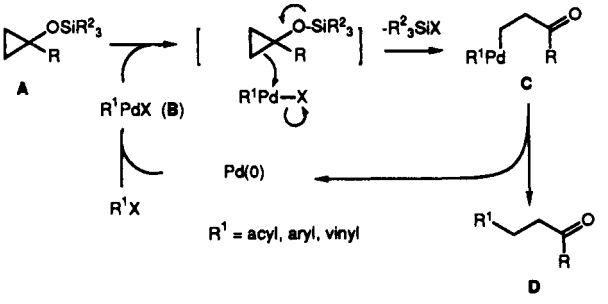
Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

Received November 27, 1990

The reaction of a variety of siloxycyclopropanes with acid chlorides in the presence of a catalytic amount of a palladium/phosphine complex gives 1,4-dicarbonyl compounds to good yield. 1-Alkoxy-1-(trialkylsiloxy)-cyclopropanes react with both aromatic and aliphatic acid chlorides in chloroform to give 1,4-keto esters. Synthesis of 1,4-diketones by the acylation of 1-alkyl- or 1-aryl-1-siloxycyclopropanes has been achieved by carrying out the reaction if HMPA under 10–20 atm of carbon monoxide. Kinetics studies and product analysis revealed the unique mechanism of this reaction, which involves rate-determining cleavage of the strained cyclopropane carbon–carbon bond with a coordinatively unsaturated acylpalladium chloride complex. Ab initio calculations of hydroxylated cyclopropane model compounds showed that the unique reactivities of the siloxycyclopropanes may be correlated with the molecular orbital properties of these compounds rather than their ground-state structural properties.

Since the preparation of platinacyclobutanes by the reaction of cyclopropanes with a platinum(II) complex[1] and their subsequent characterization,[2] activation of carbon–carbon σ-bonds by homogeneous transition-metal complexes has been extensively studied in relation to the preparation of stable metal complexes[3] and metal-catalyzed rearrangement of strained molecules.[4] However, the potential of the C–C bond activation in organic synthesis, especially, with regard to its use for intermolecular C–C bond formation, has been little explored, and only a few catalytic C–C bond forming reactions between highly strained molecules and low molecular weight molecules[5] have been recorded as successful examples of such endeavors. It has thus remained a challenge for synthetic and organometallic chemists to develop metal-catalyzed reactions that effect an intermolecular C–C bond formation

Scheme I



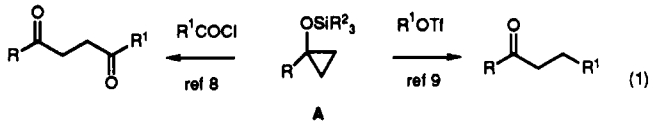
† Adjunct professor at Institute for the Molecular Science, Okazaki National Research Institutes.

(1) Tipper, C. F. H. *J. Chem. Soc.* **1955**, 2043.

0022-3263/91/1956-2809$02.50/0

coupled with the cleavage of a C–C bond.

With such a background in mind, we have focused for sometime on the metal-mediated reactions of electron-rich cyclopropanes[6,7] and recently found the palladium-catalyzed reactions of siloxycyclopropanes (A) with acid chlorides,[8] aryl triflates,[9] and vinyl triflates[10] (eq 1) wherein



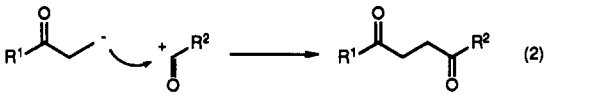
A

R = H, alkyl, aryl, alkoxy R^1 = aryl, vinyl

both the cyclopropane ring cleavage and the C–C bond formation have been achieved in a single catalytic process. On the basis of preliminary mechanistic studies of these reactions, we have proposed a working mechanism[9] (Scheme I) wherein an electrophilic organopalladium(II) species (B) cleaves the cyclopropane ring[11] and the resulting intermediate (C) undergoes reductive elimination to give the final product (D).

Synthetically, these reactions have shown that siloxycyclopropanes serve as useful, stable synthons of homoenolates of esters, ketones, and aldehydes in their *catalytic* chemistry,[6,12] as enol silyl ethers play an equivalent role in enolate chemistry,[13] thus significantly expanding the utility of the homoenolate methodology that had been studied mainly for the stoichiometric ester homoenolates.[6,14-16]

We considered that the palladium-catalyzed acylation of siloxycyclopropanes (R^1X = acid chloride in Scheme I) that we reported recently[8] merits detailed synthetic and mechanistic studies: Firstly, this acylation reaction has provided a new catalytic route to synthetically important 1,4-dicarbonyl compounds, making use of a retrosynthetic dissection characteristic to homoenolate chemistry (eq 2).

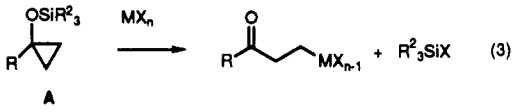


Secondly, the kinetic studies described in the following text have shown that this reaction represents a unique synthetic process that involves catalytic C–C bond activation. We describe, in this article, the synthetic and mechanistic details of this palladium-catalyzed acylation reaction as well as the ab initio quantum mechanical studies on the molecular orbitals and structural properties of the starting materials, the siloxycyclopropanes A.

Quantum Chemical Methods

MNDO calculations were performed by using the standard program options.[17] The ab initio calculations were carried out with the GAUSSIAN 82 program.[18] All geometries were optimized within the specified symmetry with use of 3-21G basis sets[19] and the gradient method incorporated as standard program options.

Ab Initio MO Studies of Hydroxycyclopropanes. In the reaction of a d transition metal with a C–C s bond of an alkane, it is the σ-orbital of the C–C bond that strongly interacts with the vacant orbital of the metal, since the σ^*-orbital is too high in energy to become available for the interaction with the filled orbitals of the metal.[20] Owing to a semiconjugative interaction between the strained C–C bond and the oxygen lone pairs in A (vide infra), the cyclopropane ring of a siloxycyclopropane is much more nucleophilic than the parent cyclopropane. Thus, siloxycyclopropanes,[14a,21] being stable and readily available, are ideal substrates for the studies of their interaction with electrophilic metal complexes. In fact, such a reaction yields a variety of β-metallo carbonyl compounds (metal homoenolates) (eq 3).[14,22] The siloxycyclopropane route



A

(2) Adams, D. M.; Chatt, J.; Guy, R. G.; Sheppard, N. *J. Chem. Soc.* **1961**, 738. Bailey, N. A.; Gillard, R. D.; Keeton, M.; Mason, R.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1966**, 396. Binns, S. E.; Cragg, R. H.; Gillard, R. D.; Heaton, B. T.; Pillbrow, M. F. *J. Chem. Soc. A* **1969**, 1227.

(3) (a) For a review, see: Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. For some pertinent examples, see: (b) Kang, J. W.; Moseley, R.; Mailtlis, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. (c) Casser, L.; Halpern, J. *J. Chem. Soc. D* **1971**, 1071. (d) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (e) Moriaty, R. M.; Chen, K.-N.; Churchill, M. R.; Chang, S. W.-Y. *J. Am. Chem. Soc.* **1974**, *96*, 3661. (f) Eilbracht, P. *Chem. Ber.* **1976**, *109*, 1429. (g) Hoberg, H.; Herea, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 877. (h) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054. (i) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1260. (j) Flood, T. C.; Statlar, J. A. *Organometallics* **1984**, *3*, 1795. (k) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222. (l) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976. (m) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717. (n) Takahashi, T.; Tamura, M.; Saburi, M.; Uchida, Y.; Negishi, E.-i. *J. Chem. Soc., Chem. Commun.* **1989**, 852.

(4) For a review, see: Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.

(5) (a) Noyori, R.; Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *92*, 5780. (b) Noyori, R.; Kumagai, Y.; Takaya, H. *J. Am. Chem. Soc.* **1974**, *96*, 634. (c) Inoue, Y.; Hibi, T.; Satake, M.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* **1979**, 982. (d) Lewis, R. T.; Motherwell, W. B.; Shipman, M. *J. Chem. Soc., Chem. Commun.* **1988**, 948. (e) Yamago, S.; Nakamura, E. *J. Chem. Soc., Chem. Commun.* **1988**, 1112.

(6) (a) Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1987**, *109*, 8056. (b) Nakamura, E.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1986**, *108*, 3745. (c) Nakamura, E.; Kuwajima, I. *Org. Synth.* **1987**, *65*, 17.

(7) For our recent work in a related field, see: (a) Nakamura, E.; Isaka, M.; Matsuzawa, S. *J. Am. Chem. Soc.* **1988**, *110*, 1297. (b) Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1989**, *111*, 7285. (c) Isaka, M.; Matsuzawa, S.; Yamago, S.; Ejiri, S.; Miyachi, Y.; Nakamura, E. *J. Org. Chem.* **1989**, *54*, 4727.

(8) Aoki, S.; Fujimura, T.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1989**, *30*, 6541.

(9) Aoki, S.; Fujimura, T.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1988**, *110*, 3296.

(10) Unpublished results by T. Fujimura in these laboratories.

(11) (a) Theoretical analysis: Blomberg, M. R. A.; Sieghahn, P. E. M.; Bäckfall, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 4450 and references therein. (b) Ouellette, R. J.; Levin, C. *J. Am. Chem. Soc.* **1971**, *93*, 471.

(12) Oshino, H.; Nakamura, E.; Kuwajima, I. *J. Org. Chem.* **1985**, *50*, 2802.

(13) Kuwajima, I.; Nakamura, E. *Acc. Chem. Res.* **1985**, *18*, 181.

(14) (a) Kuwajima, I.; Nakamura, E. *Top. Curr. Chem.* **1990**, *155*, 1. (b) Nakamura, E. *J. Synth. Org. Chem. Jpn.* **1989**, *47*, 931. (c) Ryu, I.; Sonoda, N. *J. Synth. Org. Chem. Jpn.* **1985**, *43*, 112. (d) Kuwajima, I.; Nakamura, E. *Comprehensive Organic Synthesis*; Heathcock, C. H., Ed.; Pergamon Press, in press.

(15) Cf. ref 6 for pertinent references. See also: (a) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z.-i. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1157. (b) Tamaru, T.; Ochiai, H.; Nakamura, T.; Tsubaki, K.; Yoshida, Z.-i. *Tetrahedron Lett.* **1985**, *26*, 5559.

(16) (a) Fukuzawa, S.-i.; Fujinami, T.; Sakai, S. *J. Chem. Soc., Chem. Commun.* **1986**, 475. (b) Fukuzawa, S.-i.; Sumimoto, N.; Fujinami, T.; Sakai, S. *J. Org. Chem.* **1990**, *55*, 1628.

(17) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(18) Binkley, J. S.; Frisch, J. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Pople, J. A. GAUSSIAN 82; Department of Chemistry: Carnegie-Mellon University, Pittsburgh, PA, 1982.

(19) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(20) McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123.

(21) Saläun, J. *Chem. Rev.* **1983**, *83*, 619. Murai, S.; Ryu, I.; Sonoda, N. *J. Organomet. Chem.* **1983**, *253*, 121.

(22) Cf. (a) Nakamura, E.; Shimada, J.-i.; Kuwajima, I. *Organometallics* **1985**, *4*, 641. (b) Murakami, M.; Inoue, M.; Suginome, M.; Ito, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3649. Ito, Y.; Inouye, M.; Suginome, M.; Murakami, M. *J. Organomet. Chem.* **1988**, *342*, C41.

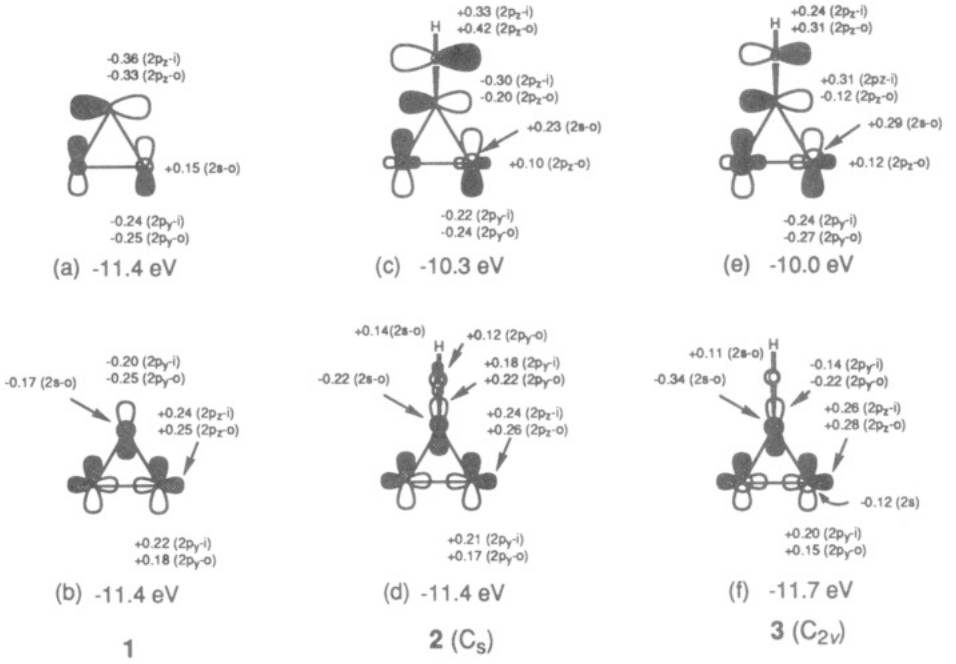
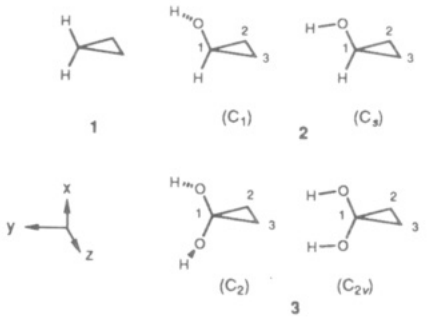


Figure 1. Highest and second highest occupied molecular orbitals of **1**, **2** (C_s), and **3** (C_{2v}). HF/3-21G energies and coefficients (>0.1) are shown.

to β-metallo carbonyl compounds has proven to be particularly suitable for the preparation of *ester* homoenolate nucleophiles from A (R = alkoxy) but generally unsuitable to prepare ketone or aldehyde derivatives,[23] owing to the low reactivities of siloxycyclopropanes lacking this alkoxy group.

Although the siloxy group is well-expected to activate the cyclopropane ring, it is not very clear a priori, however, how big such an effect may be. Hence, we investigated by theoretical means the substituent effects on the structure and the molecular orbitals of the cyclopropanes. For simplicity of the calculation, we have chosen cyclopropane (**1**), hydroxycyclopropane (**2**; C_1 and C_s *anti*-OH), 1,1-dihydroxycyclopropane (**3**; C_2 gauche and C_{2v} *anti*-OH) as models of the substrates that we have used for the experiments.



The geometries of heavy atoms and the total atomic charge obtained by HF/3-21G calculation are shown in Table I, together with the reported geometries of **1** and **2** (C_s) obtained by 4-31G,[24] DZ,[25] and MNDO[24] calculations. The HF/3-21G geometry of **2** (C_s) showed a good to excellent agreement to those obtained previously by DZ and 4-31G ab initio calculations. These geometries of **2** (C_s) showed notable shortening of C_1–C_2 bond and elongation of C_2–C_3 bond. This trend was found even more conspicuous with **3** (C_{2v}). MNDO calculation, on the other hand, indicated a reverse trend, which is probably unrealistic as has been previously pointed out by Clark[24] for **2**. It is interesting to note that, in contrast to the neutral alcohol **2**, its oxy anion (cyclopropoxide) has been calculated (DZ) to have elongated C_1–C_2 bond.[25]

The FMO energies of the molecules are also shown in Table I, and the plots of HOMOs are indicated in Figure 1. In **2** (C_s) and **3** (C_{2v}) (Figure 1c,e), the energy of an original HOMO (Figure 1b) of cyclopropane **1** is raised through an out of phase interaction with the oxygen p orbitals. The HOMO energy of the cyclopropane has been raised by 1.1 eV by the first OH substitution, and then further by 0.3 eV by the second OH group. The HOMO level of **2** (−10.3 eV) thus becomes comparable to that of ethylene. The high HOMO of **3** (−10.0 eV), which is now 1.45 eV higher than that of **1**, strongly suggests that the derivatives of **3** would make good nucleophiles, and the large coefficients of C_2, C_3, and the oxygen atom(s) in **2** and **3** suggest that these compounds will behave as potential ambident nucleophiles (as has been experimentally found[6a,12]). The orbital energy of one of the degenerate HOMO (Figure 1b) of cyclopropane remains unaffected by the OH substitution and appears as the second highest occupied orbital (Figure 1d,f) in **2** and **3**.

The gauche conformers **2** (C_1) and **3** (C_2) are more stable than the *anti*-OH conformers of higher symmetry. The former comes out to be 2.7 kcal and the latter 11.6 kcal below the respective lower symmetry conformers. Also, **2** (C_1) and **3** (C_2) have much lower HOMO levels due to less efficient conjugative effects of the oxygen p orbitals parallel to the plane of the cyclopropane (cf. Figure 1c,e) and thus are expected to be less nucleophilic.

In summary, the hydroxycyclopropanes **2** and **3** show little structural characteristics, which may suggest the likelihood for the ring opening to homoenolate-like structures. Molecular orbital properties, however, indicate that they (especially **3** (C_{2v})) will be much more susceptible to electrophilic attack than unsubstituted cyclopropane.

(23) For some important exceptions of this statement, see: Reference 15a. (a) Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192. Ryu, I.; Ogawa, A.; Sonoda, N. *J. Chem. Soc. Jpn.* **1985**, 442. See also refs 9 and 14.

(24) Clark, T.; Spitznagel, G. W.; Klose, R.; von Ragué Schleyer, P. *J. Am. Chem. Soc.* **1984**, *106*, 4412.

(25) Durmaz, S.; Kollmer, H. *J. Am. Chem. Soc.* **1980**, *102*, 6942.

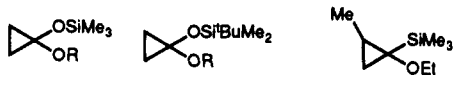
Table I. Geometries and Atom Charge of Substituted Cyclopropanes

compd		geometry (Å) 3-21G	4-31G[a]	DZ[b]	MNDO		HF/3-21G total atom. charge	HOMO (eV)	LUMO (eV)	total energy (au)
1	CC	1.513	1.502	1.513	1.525	C	−0.45	−11.41	7.54	−116.401 21
2 (C_1)	C_1C_2	1.506				C_1	+0.055	−10.81	7.23	−190.832 58
	C_2C_3	1.521				C_2	−0.48			
	C_1C_3	1.492				C_3	−0.45			
	C_1O	1.418				O	−0.67			
2 (C_s)	C_1C_2	1.497	1.492	1.498	1.540[c]	C_1	+0.060	−10.30	6.73	−190.828 22
	C_2C_3	1.525	1.517	1.525	1.525	C_2	−0.46			
	C_1O	1.423	1.408	1.429	1.381	O	−0.68			
3 (C_2)	C_1C_2	1.485				C_1	+0.53	−10.80	7.41	−265.283 22
	C_2C_3	1.538				C_2	−0.45			
	C_1O	1.399				O	−0.69			
3 (C_{2v})	C_1C_2	1.483			1.552	C_1	+0.56	−9.99	6.25	−265.264 70
	C_2C_3	1.545			1.529	C_2	−0.45			
	C_1O	1.412			1.386	O	−0.70			

[a] Reference 23. [b] Reference 24. [c] The geometries of 2 (C_s) are taken from ref 23.

The first hydroxy substitution effects strong semiconjugative activation of the cyclopropane ring, and the effect of the second substitution is substantially larger; therefore, the derivatives of 3 (i.e., A, R = alkoxy) will be more reactive toward an organometallic electrophile (B) than those of 2.

Synthesis of 4-Keto Esters. 4-Keto esters (R^1 = alkoxy in eq 2) are among important classes of carbonyl compounds[26] and serve as precursors to a variety of organic compounds including carbocycles and heterocycles. The classical synthesis of these compounds relying on the coupling of an enolate anion and an enolonium cation equivalent has not been as successful as it was hoped to be.[26i] Of the retrosynthetic dissections cleaving the C_3–C_4 bond, the conjugate addition of an acyl anion equivalent to a Michael acceptor has been explored for some time,[27] but the retrosynthetic cleavage that generates a homoenolate anion (eq 2) is a relatively unexplored possibility, the investigation of which was started only recently through the use of stoichiometric homoenolate chemistry.[14]

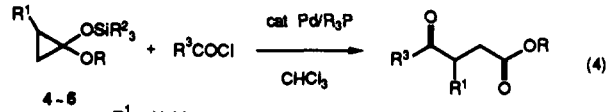


4a: R = Et
b: R = iPr

5a: R = Et
b: R = iPr

6

A metal-catalyzed reaction of 1-alkoxy-1-(trialkylsiloxy)-cyclopropanes 4–6 with acid chlorides will produce 4-keto esters (eq 4). We have chosen this reaction as an initial



(4)

4–6

R^1 = H, Me
R^3 = alkyl, aryl

7a: R^1 = H
b: R^1 = Me

target of our studies. The starting materials (4–6)[14a] are available on a large scale from β-halopropionate esters[28] or from enol silyl ethers via Simmons–Smith reaction.[29,6b] The prototypal compound 4a is now commercially available (Aldrich).

Table II. Solvent Effects in the 4-Keto Ester Synthesis (Eq 4)[a]

entry	solvent[b]	% yield[c] 2.5 h	15 h
1	DMA	11	77
2	PrCN	20	90
3	HMPA	20	38
4	$ClCH_2CH_2Cl$	34	97
5	THF	13	76
6	$CHCl_3$	99	100
7	C_6H_6	13	72

[a] The reaction was performed with 2 equiv of 4b in the presence of 5 mol % of $PdCl_2(PPh_3)_2$ (8) at 60–70 °C. [b] Shown in the order of decreasing dielectric constant. [c] Yield based on benzoyl chloride (GLC).

Table III. Effects of the Palladium Catalyst (Eq 4)[a]

entry	catalyst	% yield[b] 2.5 h	15 h
1	$PdCl_2$	<1	
2	$PdCl_2(Ph_3P)_2$ (8)	99	100
3	$PdCl_2(o\text{-}Tol_3P)_2$	85	97
4	$Pd(PhCO)Cl(Ph_3P)_2 \cdot CH_2Cl_2$ (9)	100	
5	$Pd(Ph_3P)_4$	1	100
6	$PdCl_2(Ph_3P)_2$ + excess Ph_3P	0	
7	$NiCl_2(Ph_3P)_2$ + 2DIBAH	0	

[a] The reaction was performed in $CHCl_3$ by using of 2 equiv of 4b with 5 mol % of the catalyst at 60–70 °C. [b] Yield based on benzoyl chloride (GLC).

Initial optimization of the reaction conditions was carried out for the reaction of 1-ethoxy-1-(trimethylsiloxy)-cyclopropane (4a, 2 equiv) with benzoyl chloride at 60–70 °C in the presence of 5 mol % of $PdCl_2(PPh_3)_2$ (8). The final yields were generally high (>70%) regardless of the reaction medium (Table II). Chloroform was found to be the solvent of choice, giving essentially a quantitative yield in a minimal reaction period (2 h, 70 °C). Solvents of higher basicity were found to slow down the reaction, whereas the polarity of solvents had little effects on the rate or on the yield (Table II). In no cases could we find the products due to O-acylation[6,12] (i.e., (benzoyloxy)-cyclopropane).

(26) For some previous syntheses of 1,4-dicarbonyl compounds, see: (a) McMurry, J. E.; Melton, J. *J. Am. Chem. Soc.* **1971**, *93*, 5309. (b) Stetter, H.; Schreckenberg, M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 81. (c) Stork, G.; Maldonado, L. *J. Am. Chem. Soc.* **1974**, *96*, 5272. (d) Miyashita, M.; Yanami, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1976**, *98*, 4679. (e) Shimada, J.-i.; Hashimoto, K.; Kim, B. H.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 1759. (f) Welch, S. C.; Chayabunjonglerd, S. *J. Am. Chem. Soc.* **1979**, *101*, 6768. (g) Sato, T.; Okazaki, H.; Otera, J.; Nozaki, H. *J. Am. Chem. Soc.* **1988**, *110*, 5209. (h) For a conventional approach, see: Warren, S. *Organic Synthesis: The Disconnectin Approach*; John Wiley & Sons: Chichester, 1982; Chapter 25.

(27) Cf. Stetter, H.; Schreckenberg, M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 81.

(28) Saläun, J.; Maruguerite, J. *Org. Synth.* **1984**, *63*, 147. Fadel, A.; Canet, J.-L.; Saläun, J. *Synlett* **1990**, *89* and references therein.

(29) Rousseaux, G.; Slougui, N. *Tetrahedron Lett.* **1983**, *24*, 1251.

Table IV. 1,4-Keto Esters by Acylation of Ester Homoenolates[a]

entry	siloxycyclopropane	R	R^1	SiR^2_3	acid chloride R^3COCl	catalyst[b]	% yield[c]
1	**5b**	O-*i*-Pr	H	Si-*t*-BuMe$_2$	C_6H_5COCl	**9**	97
2	**4b**	O-*i*-Pr	H	$SiMe_3$	C_6H_5COCl	**9**	90
3	**4b**	O-*i*-Pr	H	$SiMe_3$	$(C_6H_5CO)_2$	**8**	0
4	**4b**	O-*i*-Pr	H	$SiMe_3$	C_6H_5COBr	**8**	0
5	**5a**	OEt	H	Si-*t*-BuMe$_2$	*p*-ClC_6H_4COCl	**9**	83
6	**4a**	OEt	H	$SiMe_3$	C_6H_5COCl	**8**	71
7	**4a**	OEt	H	$SiMe_3$	*p*-$MeOC_6H_4COCl$	**9**	86[d]
8	**4a**	OEt	H	$SiMe_3$	(*E*)-C_6H_5CH=$CHCOCl$	**8**	24[e]
9	**5a**	OEt	H	Si-*t*-BuMe$_2$	$CH_3(CH_2)_{10}COCl$	**8**	46
10	**4a**	OEt	H	$SiMe_3$	$C_6H_5CH_2CH_2COCl$	**8**	45[d]
11	**5b**	O-*i*-Pr	H	Si-*t*-BuMe$_2$	$C_6H_5CH_2CH_2COCl$	**14**	83
12	**4a**	OEt	H	$SiMe_3$	CH_3CH_2COCl	**14**	68
13	**6**	OEt	Me	$SiMe_3$	C_6H_5COCl	**9**	86
14	**6**	OEt	Me	$SiMe_3$	*p*-ClC_6H_4COCl	**8**	93[e]
15	**6**	OEt	Me	$SiMe_3$	*p*-$MeOC_6H_4COCl$	**8**	85
16	**6**	OEt	Me	$SiMe_3$	$CH_3(CH_2)_{10}COCl$	**8**	37
17	**6**	OEt	Me	$SiMe_3$	$C_6H_5(CH_2)_2COCl$	**8**	42

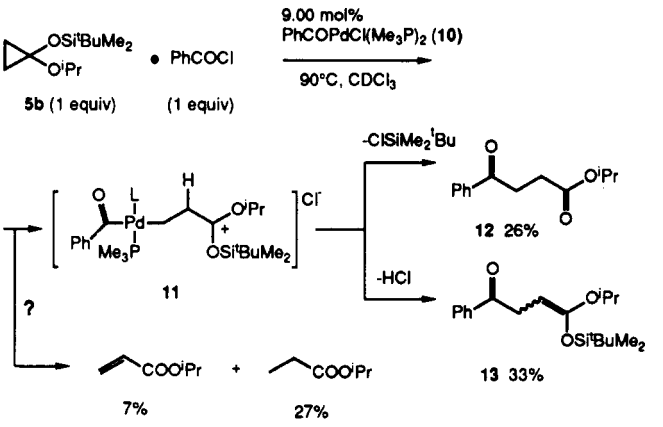
[a] The reaction was performed with 1 equiv each of the reactants (unless noted otherwise) at 90–100 °C in the presence of 1–5 mol % of the catalyst. [c] Isolated yield. [d] Slight excss (1.2 equiv) of the cyclopropane was used. [e] 2 equiv of the cyclopropane was used.

Examination of the catalyst indicated the following trends (Table III): (1) Pd(II)$(R_3P)_2$ complexes (R = Ph, PhO) are effective catalysts (entries 2–4), whereas $PdCl_2$ itself (entry 1) and Ni/Ph_3P complexes (entry 7) are totally ineffective. (2) As examined for the catalysts having Ph_3P as a ligand, a phosphine/palladium ratio of 2:1 is optimum (see Figure 4). Though the reaction initially proceeds much faster with a phosphine/palladium ratio of 1:1, the catalytic system was unstable and precipitated metallic palladium. An increase of the molar ratio to 4:1 drastically retarded the reaction, but the final yield remained still excellent (entry 5). (3) The reaction rate decreases as the basicity of the phosphine ligand increases, i.e., $(PhO)_3P$ > Ph_3P > Me_3P (vide infra). (4) Varying length of induction period (>30 min) was observed when $PdCl_2(Ph_3P)_2$ (**8**) was used as a catalyst, while none was observed with either $PhCOPdCl(Ph_3P)_2 \cdot CH_2Cl_2$ (**9**) or **8** previously treated with 2 equiv of DIBAL. (4) The only side reaction (except the case described in the following text) was the formation of a small amount of alkyl propionate, and this side reaction could be eliminated by the use of (*tert*-butyldimethylsiloxy)cyclopropanes **5** instead of **4**.

When the reaction of **5b** with benzoyl chloride was carried out with 9.0 mol % of $PhCOPdCl(Me_3P)_2$ (**10**), we made a mechanistically intriguing observation (Scheme II). Thus, the reaction at 90 °C for 5 h in a sealed NMR tube (analyzed by 200-MHz ^1H NMR) afforded, in addition to the keto ester **12**, a considerable amount of ketene acetal (**13**). The formation of **13** together with **12** suggests the formation of an oxonium intermediate[30] (e.g., **11**), which gives **13** upon loss of proton and **12** upon loss of the silyl group. We have previously made a similar observation in the reaction of **5b** with $TiCl_4$.[6b,22a] Isopropyl propionate formed in 27% yield accounts for the proton released by the formation of **13**. The exact stage from which the acrylate and the propionate have been produced is unclear.

The palladium-catalyzed acylation was examined for a variety of combinations of **4** or **5** with acylating agents. Air-stable and readily available $PdCl_2(Ph_3P)_2$ (**8**, 1–5 mol %) was used as a catalyst of choice. One equivalent or a slight excess of the cyclopropanes was routinely used for the reactions listed in Table IV. Benzoic anhydride and benzoyl bromide were unreactive and were recovered together with the siloxycyclopropanes (entries 3 and 4). Substituted benzoyl chlorides reacted cleanly (entries 5, 7, 14, and 15).

Scheme II



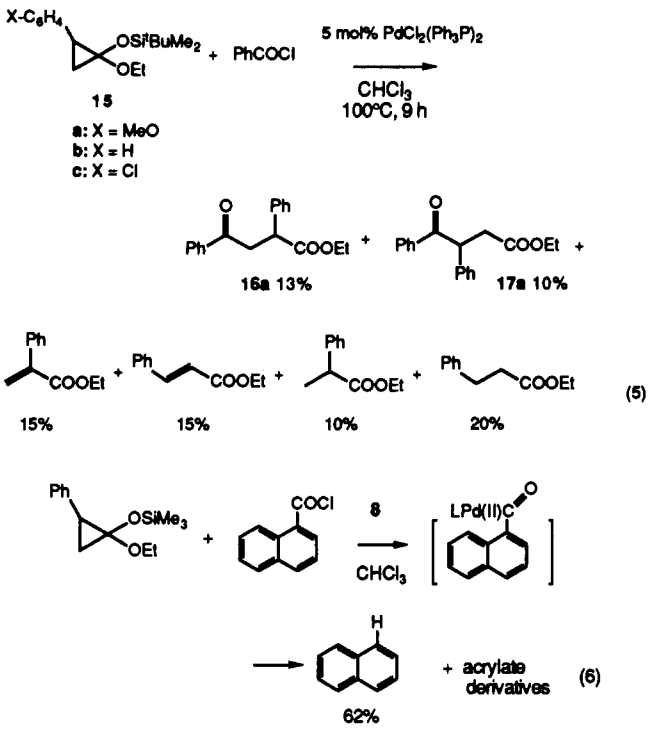
The reaction with aliphatic acid chlorides gave a complex mixture of products, from which ~40% of the desired product could be isolated. Brief reexamination of the reaction conditions showed that the yield can be significantly improved by the use of $PtCl_2(Ph_3P)_2$ (**14**) instead of the palladium catalysts (entries 10 and 11). In entries 10 and 11, we observed a trace of 1-indanone, which could have formed by intramolecular Friedel–Crafts-type cyclization of the starting acid chloride.

We next examined the effects of C_2-substituents on the siloxycyclopropane. The reaction of a 2-methyl-substituted cyclopropane **6**, which proceeded substantially slower than that of **4**, gave **7b** through exclusive cleavage of the less hindered C_1–C_3 bond (eq 4; Table IV, entries 14–17).

2-Phenyl-substituted cyclopropanes **15** reacted much slower than **4** or **5**. The reaction of (*tert*-butyldimethylsiloxy)cyclopropane **15b** with benzoyl chloride afforded a mixture of 4-keto esters **16a** and **17a**, acrylate, and propionate derivatives, each consisting of two regioisomers due to cleavage of the cyclopropane ring in two ways (eq 5). A notable side product in the reaction with naphthoyl chloride was naphthalene (62%), due to decarbonylation[31] of a naphthoylpalladium intermediate taken place at a certain stage of the catalytic cycle (eq 6). Decarbonylation was also the major reaction pathway in the reaction of

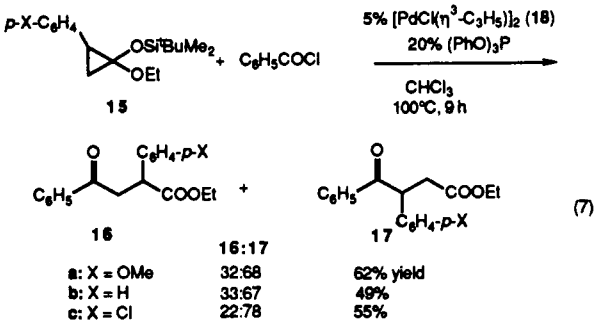
(30) For the formation of a similar cationic intermediate, see: Murai, S.; Aya, T.; Renge, T.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1974**, *39*, 858. See also ref 6b.

(31) Tsuji, J.; Ohno, K. *J. Am. Chem. Soc.* **1968**, *90*, 94.



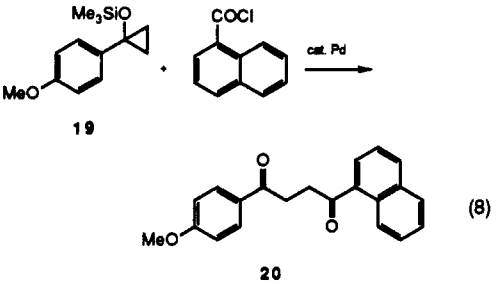
pivaloyl chloride with **4a** in the presence of 8.

Use of $(PhO)_3P$ as a ligand together with $[PdCl(\eta^3\text{-}C_3H_5)]_2$[32] (**18**) improved the yield of the desired pathway (eq 7). Thus, the reaction of 1 equiv each of the cyclo-



propane **15a** and benzoyl chloride proceeded in 49% yield to give a 2:1 mixture of products **16a** and **17a** due to C_1–C_2 and C_1–C_3 bond cleavage, respectively.[33] The regioselectivity, examined as the function of the para substituent of the phenyl group (i.e., **15a,b,c**), revealed very small substituent effects. Thus, the **16**/**17** ratio varied only between 2.0 and 3.5 as the substituent was changed from *p*-methoxy to *p*-chloro group (eq 7).

Synthesis of 1,4-Diketones. Extension of the previous chemistry to the synthesis of 1,4-diketones (eq 2; R^1, R^2 = alkyl or aryl) was our logical second objective.[34] Although a number of useful syntheses of this class of compounds have been recorded in the literature, none based on metal homoenolate chemistry has been reported until a recent publication by Yoshida and Tamaru.[35] Before this report, ketone homoenolates had been considered to be too unstable, rapidly cyclizing to cyclopropanolates.[36] The Tamaru–Yoshida paper, however, also underscored the thermal sensitivity of such species relative to the corresponding ester homoenolates. Therefore, a catalytic synthesis of 1,4-diketones through the siloxycyclopropane route (see eq 8) appeared to be a particularly appealing synthetic strategy.



The siloxycyclopropanes needed for this purpose (e.g., **18**) would have moderately high-lying HOMO (vide supra) and were deemed less reactive than **4**–**6**. In fact, we soon realized that the optimum conditions found for the keto ester synthesis gave none of the desired diketones. We examined the reaction of 1-(4-methoxyphenyl)-1-(trimethylsiloxy)cyclopropane (**19**) and naphthoyl chloride in some detail. Although we quickly found that the use of HMPA was essential to obtain diketone **20**, we could not improve the yield beyond 30% under a variety of reaction conditions. During the course of the investigations, we noticed the formation of a considerable amount of naphthalene (cf. eq 6), which is most probably the result of decarbonylative decomposition of a naphthoyl palladium intermediate. To suppress this side reaction, we employed a CO atmosphere for the reaction. Thus, the reaction carried out in HMPA under 10–20 atm of CO consistently gave the diketone in >50% yield. Use of higher pressure gave a better yield of the product in larger scale experiments. As in the low-yielding cases of the 4-keto ester synthesis, the use of a catalyst (ca. 5 mol %, a Pd:P ratio = 1:2) prepared in situ from $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (**18**) and $(PhO)_3P$ further improved the yield.

Under the optimized conditions, the reaction was found to be applicable to various combinations of siloxycyclopropanes and aromatic acid chlorides, and the results are summarized in Table V. In spite of the rather severe thermal conditions, we found no evidence for the decomposition of the diketone products. The reaction with aliphatic and α,β-unsaturated acid chlorides failed under a variety of conditions (entries 9, 12, and 13). Some attempts to prepare 4-keto aldehydes by the reaction of siloxycyclopropanes (A, R = H) also failed.

Kinetic Studies. Having studied the synthetic aspects of the palladium-catalyzed acylation reactions, we proceeded to examine the mechanism of the catalytic reactions. A large body of data in organopalladium chemistry supported the main framework of the proposed mechanistic scheme (Scheme I) that basically assumes a standard Pd(II)/Pd(0) catalytic cycle.[37] Oxidative addition involving $Pd(Ph_3P)_2$ and 1,1-reductive elimination are reactions reasonably well understood.[37] The most interesting unit reaction in this scheme is the mechanistic pathway connecting B and D, which would involve the interaction between A, and B, the formation of a dialkylpalladium

(32) $[PdCl(\eta^3\text{-}C_3H_5)]_2$: Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.

(33) For regiochemistry of the cyclopropane ring cleavage in a related stoichiometric reactions, see ref 6.

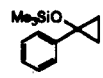
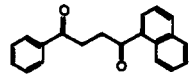
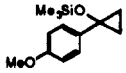
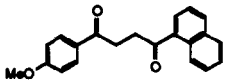
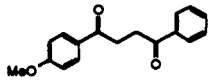
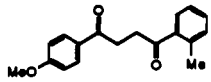
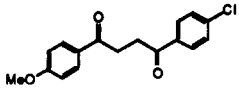
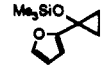
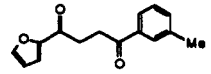
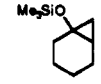
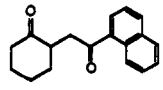
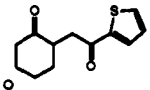
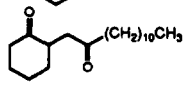
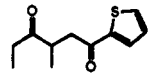
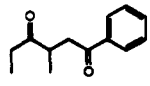
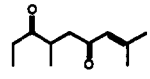
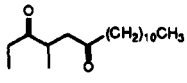
(34) We have recently developed yet another palladium-catalyzed synthesis of 1,4-diketones that involves coupling of a siloxycyclopropane, an aryl triflate, and CO; manuscript in preparation.

(35) Zinc homoenolates of ketones have been prepared by reduction of 3-iodo ketones with metallic zinc and reacted with acid chlorides (ref 15a).

(36) Cf. Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 205.

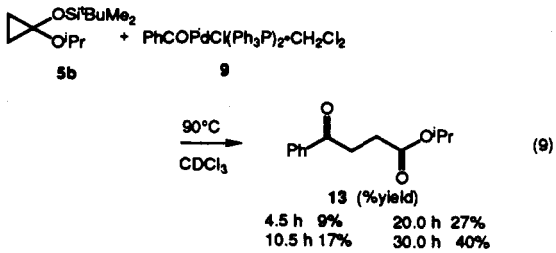
(37) For the studies of palladium-catalyzed acylation reactions that involves transmetallation, see: Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6129 and references therein.

Table V. 1,4-Diketones by Acylation of Ketone Homoenolates[a]

entry	cyclopropane	acid chloride	1,4-diketone	% yield[b]
1		1-$C_{10}H_7COCl$		53[c,d]
2	 19			69
3		C_6H_5COCl		75
4		2-MeC_6H_4COCl		77
5		4-ClC_6H_4COCl		55
6		3-MeC_6H_4COCl		52
7		1-$C_{10}H_7COCl$		46
8		2-thenoyl chloride		46
9		$CH_3(CH_2)_{10}COCl$		0
10		2-thenoyl chloride		56
11		C_6H_5COCl		42
12		$(CH_3)_2C=CHCOCl$		0
13		$CH_3(CH_2)_{10}COCl$		0

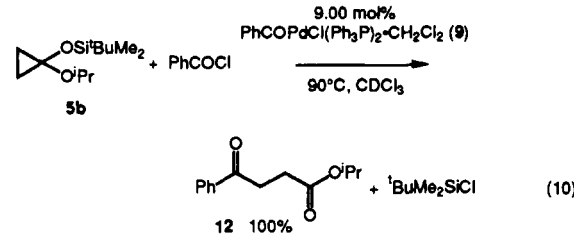
[a] The reaction was performed in the presence of 18 and $(PhO)_3P$ (2.5–10 mol % of Pd). [b] Isolated yield. [c] $PdCl_2(PPh_3)_2$ (8) was used as a catalyst. [d] 1.5 equiv of the cyclopropane was used.

species C, and its reductive elimination. The feasibility of this sequence was supported by the success of a stoichiometric reaction between the siloxycyclopropane **5b** and the benzoylpalladium complex **9**. Thus, heating an equimolar mixture of **5b** and **9** (0.002 M each) at 90 °C in $CDCl_3$ gave **13** in 40% yield after 30 h. Detailed investigation of this stoichiometric reaction was precluded by the complexity of the reaction.



(9)

In order to further investigate this mechanistically intriguing catalytic reaction, we have chosen to study the reaction of 1-isopropoxy-1-(*tert*-butyldimethylsiloxy)-cyclopropane (**5b**) with benzoyl chloride (eq 10). For the



(10)

standard kinetic experiments, we employed the conditions similar to those used for our preparative reaction. Preliminary studies using the method of initial rates suggested the reaction rate is first-order to **5b** and zero-order to benzoyl chloride. Since the irregularity of the reaction rate at the beginning (presumably due to temperature equilibration and/or establishment of the catalytic cycle) precluded any further detailed analysis based on the initial rates, we performed the analysis of the integrated rate equations using Gauss–Newton least-squares curve-fitting method for the data excluding some initial data points (typically 15 min).

We monitored the reaction rate with 200-MHz proton NMR for the reactions at 90 °C $CDCl_3$ with 0.60 M each of **5b** and benzoyl chloride in the presence of $(PhCO)PdCl(Ph_3P)_2 \cdot CH_2Cl_2$ (**9**; 1.0–9.5 mol % based on **5b**); the keto ester **12** and *tert*-butyldimethylsilyl chloride formed in 98–100% yield (95% isolated yield of **12**). The reaction under these conditions turned out to very cleanly follow first-order kinetics after stationary reaction was achieved until 95–98% conversion of the reactants. Variation of the initial concentration of benzoyl chloride (0.60–1.20 M) revealed that the reaction is zero order to the acid chloride and thus showed that the reaction is first order to the cyclopropane **5b** with a first-order rate constant k^1 defined in eq 11.

$$d[12]/dt = -k^1[5b] \quad (11)$$

In order to determine the effect of the catalyst concentration on k^1, the initial concentration of **9** was varied from 2.4×10^{-2} to 8.1×10^{-2} M (4.0–13.5 mol % to **5b**). In each run, excellent first-order kinetics were observed. Least-squares fitting of the dependence of k^1 on the concentration of **9** indicated the relationship in eq 12 with $k^2 = 9.3$

$$k^1 = k^2[9]^{0.44} \quad (12)$$

$\times 10^{-2}$ $M^{-0.44}$ min^{-1}. The constant k^2 reflects the reactivity of a particular siloxycyclopropane. The values of k^2 for other substrates discussed later are summarized in Table IX.

In the light of the relatively large HOMO coefficients and the total atomic charge of the oxygen atoms in hydroxycyclopropanes (Figure 1, Table I), one may suspect the operation of an alternative mechanism that involves an initial silicon to palladium transmetalation taking place through electrophilic cleavage of the Si–O bond. This mechanism is unlikely since the *tert*-butyldimethylsilyl–oxygen bond may not cleave under the mild conditions employed.[38] If such a mechanism were indeed operating for **5b** as a rate-limiting stage, however, we should be able to observe a significantly faster rate when the trimethyl-

(38) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; p 95.

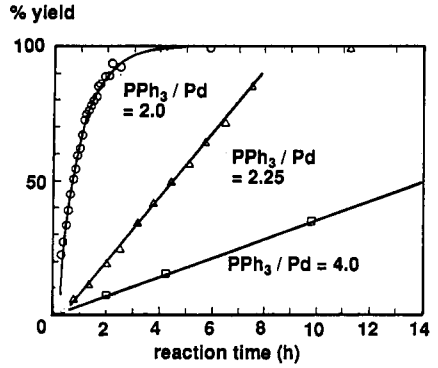


Figure 2. Effects of phosphine ligands. The catalyst/substrate is fixed at 4 mol %. Initial concentrations: $[\mathbf{5b}]_0 = [PhCOCl]_0 = 0.60$ M, $T = 90$ °C; (a) $[\mathbf{9}]_0 = 0.024$ M (phosphine/Pd = 2:1). (b) $[\mathbf{9}]_0 = 0.024$ M, $[Ph_3P]_0 = 0.006$ M (phosphine/Pd = 2.25:1). (c) $[Pd(Ph_3P)_4]_0 = 0.024$ M (phosphine/Pd = 4:1).

siloxy compound **4b** is used in place of **5b**, since, in the acidic or basic cleavage of the Si–O bond of a silyl ether of RMe_2SiOR^1 type, change of the R group on the silicon atom from *tert*-butyl to methyl accelerates the reaction rate by a factor of as much as 10^4.[38]

The same set of the reaction conditions examined for **5b** was investigated for **4b**. The reaction was quantitative (94% isolated yield), and the rate expression fitted well in eq 11 with $k^2 = 7.1 \times 10^{-2}$ $M^{-0.44}$ min^{-1}. This rate constant, which is of the same order of the magnitude of that for **5b**, clearly shows that the cleavage of the Si–O bond is not involved in the rate-limiting step.

Substituents on the cyclopropane ring significantly retard the reaction as observed qualitatively for 2-methyl-**6** and 2-phenyl-substituted derivatives **15**. More quantitatively, the reaction of 1-ethoxy-1-(trimethylsiloxy)-2-methylcyclopropane (**6**) with 1 equiv of benzoyl chloride in the presence of 9.00 mol % of **9** proceeded with $k^2 = 1.3 \times 10^{-2}$ $M^{-0.44}$·min^{-1} (i.e., >5 times slower than **4b**).

The molar ratio of the phosphine ligand relative to palladium is among important determinants of the reaction rate: when the reaction (4.0 mol % of **9**) was conducted with an additional 1.0 mol % of Ph_3P (net Ph_3P:Pd ratio = 2.25:1), the reaction slowed down considerably (Figure 2). The reaction in the presence of 4.0 mol % of Pd $(Ph_3P)_4$ proceeded even more slowly and completed only after 24 h. Notably, in both of the latter cases, the reactions were no more first order but roughly zero order, suggesting the change of the rate-limiting step of the catalytic cycle.

The nature of the phosphine ligand was also found to affect the reaction rate. The reactions catalyzed by $PhCOPdCl[(PhO)_3P]_2$ (**21**), which gave the keto ester **12** in quantitative yield with $k^2 = 4.7 \times 10^{-1}$ $M^{-0.44}$ min^{-1}. The reaction with $PhCOPdCl(Me_3P)_2$ (**10**), on the other hand, was much slower, giving a mixture of **12** and **13** as shown in Scheme II. Since **12** and **13** presumably arise from a common intermediate **11**, the sum of the rates of the formation of **12** and **13** was taken to obtain a rate constant of $k^2 = 1.9 \times 10^{-2}$ $M^{-0.44}$ min^{-1} (even if **11** is the origin of *all* esters in Scheme II, k^2 will still be 2.7×10^{-2} $M^{-0.44}$ min^{-1}). Consequently, the reaction with the most electrophilic catalyst **21** proceeds ~25 times faster than that with the least electrophilic **10**.

The effects of the substituent on an acylating agent was examined for the acylation of **5b** with substituted benzoyl chloride having *p*-Me, *p*-MeO, *p*-Cl, and *m*-NO_2 groups in the presence of 9.0 mol % of **9** at 90 °C in $CDCl_3$. All reactions were nearly quantitative, and the rate constants k^2 fell in a very small range of $(7.2–9.9) \times 10^{-2}$ $M^{-0.44}$ min^{-1} (see Table IX), affording a negligibly small ρ value ($\rho = -0.02$).

Table VI. C=O Stretching Frequencies of Para-Substituted Benzoylpalladium Complexes (23: p-$XC_6H_4COPdY(PR_3)_2$)

entry	X	Y	PR_3	$\nu_{C=O}$[a] (cm^{-1})	source
1	H	Cl	$(PhO)_3P$ (**21**)	1675	this work
2	H	Cl	Ph_3P (**9**)	1659	this work
3	H	Cl	Me_3P (**10**)	1637	this work
4	H	Br	Ph_3P	1650	ref 42
5	CF_3	Br	Ph_3P	1654	ref 42
6	CN	Br	Ph_3P	1653	ref 42
7	NO_2	Br	Ph_3P	1649	ref 42

[a] Determined for powder in paraffin.

Discussion

The rate equation shown in eq 11 is consistent with the mechanism that the cyclopropane interacts with a reactive palladium species that has been generated through a mobile equilibrium from a less reactive precursor (eq 13).

$$\mathbf{5b} + \mathbf{22} \xrightarrow{\text{slow}} \text{product} \qquad \mathbf{22} \xrightleftharpoons{\text{fast}} PhCOPdCl(Ph_3P)_2 \quad (13)$$

This reactive species is undoubtedly a benzoylpalladium complex of some kind. The feasibility of this mechanism has been verified experimentally by the stoichiometric acylation of **4b** with the **9** (eq 9). The fact that only a small increase of the Ph_3P/Pd ratio from 2 to 2.25 caused not only drastic rate retardation, but the change of the kinetics from first order to zero order (Figure 2) implies that free phosphine is involved in the step forming the reactive catalyst. Hence, a two-stage reaction (eq 13) involving the formation of a coordinatively unsaturated benzoylpalladium species **22** is consistent with these observations.[39] Sluggishness of the reaction in highly basic solvents (Table II) also supports the importance of a coordinatively unsaturated species.

With a general view of the rate-limiting step established, the details of the mechanism are then to be addressed. One of the most crucial questions is what part of the siloxycyclopropane has a productive interaction with the catalytically active species. Near equality of the reaction rates observed for **4b** and **5b** indicates that the Si–O bonding remains intact in the transition state of the rate-limiting step (cf. eq 12) and suggests instead that the C–C bond is being cleaved. This view is further supported by the large rate retardation caused by the cyclopropyl ring substitutents, which would directly hinder the interaction of the active catalyst with the cyclopropane ring.

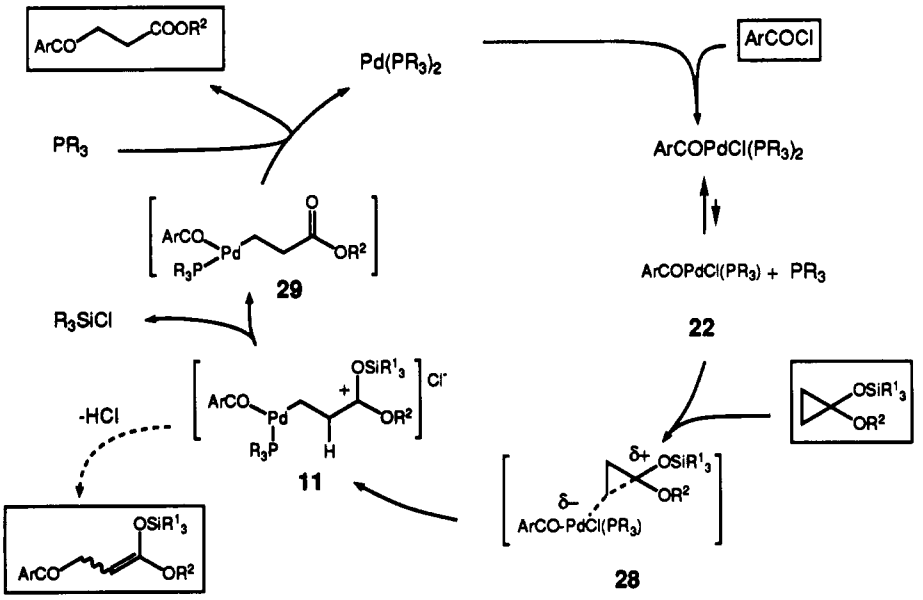
The ligands on a metal complex significantly alter the electronic nature of the center metal, thus changing not only the reactivities of the complex, but its spectral properties. There are three ligands on the putative catalytically active species **22**, which have been varied to probe their effects.

Our observation that the change of the phosphine ligand[40] from $(PhO)_3P$ to Ph_3P then to Me_3P slowed down

(39) The rate equation (11) is also consistent with a scheme that assumes the generation of (two molecules of) **22** from a dimeric acylpalladium chloride, $[(PhCOPdCl(Ph_3P)]_2$, which in turn forms from **9** upon loss of one molecule of Ph_3P. This scheme, however, is inconsistent with the dramatic rate retardation caused by the presence of even a slight excess of Ph_3P (note that there already exists in solution one equivalent of Ph_3P, which forms at the stage that generates the dimer in question) or the observed consistency of the rate equation over a 9-fold change of the initial concentration of the palladium catalyst (Figure 2).

(40) Cf. Dauben, W. G.; Keilbania, A. J., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 7345.

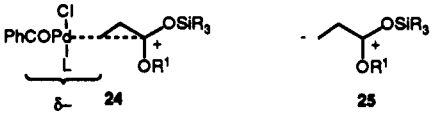
Scheme III



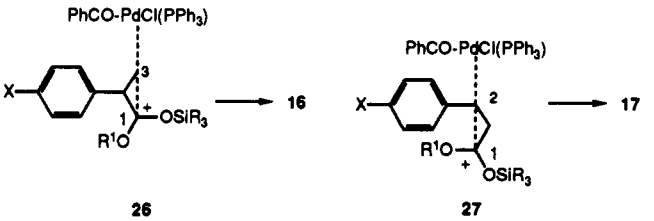
the reaction ~5 times for each change is in line with the idea that the electrophilic nature of the palladium complex is important to achieve successful C–C bond activation.

The IR frequency of the carbonyl stretching of a para-substituted benzoylpalladium complex **23** provides a measure of the electronic nature of the complex, since there exists strong conjugation between the palladium d orbital and the carbonyl π^* orbital.[41] In Table VI are compiled the IR data of para-substituted benzoylpalladium chlorides and bromides.[42] As is seen in entries 1-3, the frequency decreases as the basicity of the phosphine is increased, which indicates decreased bond order of the carbonyl double bond and in turn reflects the increased π-electron donation to the carbonyl carbon from the metal center. It is notable that the para substituents on the benzoyl group have negligible effects (entries 4–6), which is in line with the lack of para-substituent effects on the rate of acylation (vide supra).

We have obtained evidence for the formation of a stabilized cationic species **11** via cleavage of the C_1–C_2 bond of **5b**. On the basis of the experimental[43] and theoretical[11,44] studies of electrophilic cleavage of cyclopropanes with palladium(II) and related metal salts, and electrophilic C–C bond cleavage of a siloxycyclopropane may proceed through a "corner attack" to leave a positive charge on the C_1 carbon as shown in **24**. Under such circumstances, a strictly formal picture of **24** excluding palladium participation would suggest the development of a negative charge on the C_2 carbon as shown in **25**. We next probe whether this is really a case in **24**.



Substituent effects of the regioselectivity of the ring cleavage in the acylation of 2-arylcyclopropanes **15** (eq 7) served for the experimental evaluation of the charge distribution. The regioselectivity of the reaction of **15** depends on the energy differences between the transition states **26** and **27**, which produce **16** and **17**, respectively.



The X group on the phenyl group being electronically isolated from C_3, the energy of the transition state **26** would be rather insensitive to the variation of the X group, and therefore the regiochemistry (i.e., the **16**/**17** ratio) would be largely determined by the stability of **27**. Therefore, if there develops a significantly large charge separation as illustrated in **25**, we should observe a large substitutent effect on the **16**/**17** ratio, which is contrary to the experimental results (eq 7). Taking into account the effects of the palladium ligands (vide supra), the negative charge in **25** resides on the palladium center (**28**, Scheme III).

From the theoretical and mechanistic studies discussed previously, we have refined our initial mechanistic scheme and propose a more detailed mechanism for the present catalytic reaction (Scheme III). There is at the present moment little information available on a series of the events after the stage of **28**, for which a standard mechanistic protocol for the palladium catalysis has been assumed.[37] At the present time, therefore, problems as to the exact nature of the cationic species **11** and the 3-palladiopropionate **29** (e.g., its coordination state) are still open to question.

Summary

Ab initio molecular calculations allow the prediction that derivatives of hydroxycyclopropanes, in particular 1,1-dihydroxycyclopropanes, would be much more powerful nucleophiles than cyclopropane. Successful acylation of siloxycyclopropanes under palladium catalysis fully supported this prediction and at the same time provided a viable catalytic syntheses of 1,4-dicarbonyl compounds. Mechanistic studies have revealed that the present acy-

(41) For a review, see: Blackburn, B. K.; Daview, S. G.; Sutton, K. H.; Whittaker, M. *Chem. Soc. Rev.* **1988**, *17*, 148.
(42) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.
(43) Coxon, J. M.; Steel, P. J.; Whittington, B. I.; Battiste, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 2988 and references therein.
(44) Cf. Wiberg, K. B.; Kass, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 988. Wiberg, K. B.; Kass, S. R.; Bishop, K. C., III. *J. Am. Chem. Soc.* **1985**, *107*, 996.

Table VII. Preparation of 1,4-Keto Esters in $CHCl_3$

cyclopropane		acid chloride		Pd catalyst			
	μL, mmol		μL, mmol		mg, μmol	conditions (°C, h)	yield (mg, %)
4b	63.0, 0.30	C_6H_5COCl	34.8, 0.30	**9**	11.6, 13	90, 10	59, 90
5a	84.0, 0.36	p-ClC_6H_4COCl	38.1, 0.30	**9**	10.3, 12	90–100, 20	60, 83
4a	103.4, 0.51	p-$CH_3OC_6H_4COCl$	60.1, 0.43	**9**	7.4, 8.6	95, 7	87, 86
5a	84.6, 0.36	$CH_3(CH_2)_{10}COCl$	69.4, 0.30	**9**	5.1, 6	95. 7	40, 46
4a	121.2, 0.60	$C_6H_5CH_2CH_2COCl$	74.3, 0.50	**9**	8.6, 10	95. 10	53, 45
5b	52.7, 0.20	$C_6H_5CH_2CH_2COCl$	29.7, 0.20	**8**	8.6, 11	90, 8.5	41, 83
6b	88.2, 0.40	C_6H_5COCl	23.2, 0.20	**8**	7.0, 10	70, 15	38, 86
6b	88.2, 0.40	p-ClC_6H_4COCl	25.4, 0.20	**8**	7.0, 10	70, 27	47, 93
6b	88.2, 0.40	p-$CH_3OC_6H_4COCl$	28.0, 0.20	**8**	7.0, 10	70, 27	37, 85
6b	88.2, 0.40	$CH_3(CH_2)_{10}COCl$	46.3, 0.20	**8**	7.0, 10	65, 22	21, 37
6b	88.2, 0.40	$C_6H_5CH_2CH_2COCl$	33.7, 0.20	**8**	7.0, 10	70, 24	21, 42

lation reaction involves the palladium-mediated cleavage of a C–C σ-bond of the cyclopropane ring, and we expect that the closely related arylation[9] and carbonylative dimerization[45] reactions of siloxycyclopropanes proceed through similar mechanisms. The nature of the transition state elucidated by the kinetic studies as well as the product analysis will provide valuable information for the future studies of the C–C bond activation and the designing of useful new catalytic reactions.

Experimental Section

General Procedures. All reactions dealing with palladium compounds, unless otherwise noted, were carried out under nitrogen. Palladium catalysts were weighed quickly in air and transferred to a reaction vessel, which was filled with nitrogen by several evacuation/flush cycles. Routine chromatography was carried out as described by Still[46] with hexane/AcOEt was eluent.

^1H NMR (200-MHz) and ^{13}C NMR (50-MHz) spectra were measured for a $CDCl_3$ solution of a sample on a JEOL FX-200 instrument. Where noted, a 60-MHz ^1H NMR machine (Hitachi R24B) was also used. ^1H NMR spectra are reported in parts per million from internal tetramethylsilane, and ^{13}C NMR spectra from $CDCl_3$ (77.0 ppm). IR spectra were recorded on a Hitachi 260-10 instrument or a JASCO IR-800; absorptions were reported in cm^{-1}. Gas chromatographic (GLC) analysis was performed on a Shimadzu 4BM, 8A or 14A, machine equipped with a glass capillary columns (0.25-mm i.d. × 25 m) coated with OV-1, OV-17, or HR-1 (OV-1 equivalent).

Material. Ethereal solvents were distilled from sodium benzophenone ketyl immediately before use. CH_2Cl_2, $CHCl_3$, and $CDCl_3$ were distilled successively from P_2O_5 and K_2CO_3 under nitrogen. Hexamethylphosphoric triamide (HMPA) was distilled from calcium hydride under nitrogen and stored over molecular sieves. Siloxycyclopropanes were prepared as previously described.[6,28,29] For kinetic studies, $CDCl_3$ was further purified by overnight storage over P_2O_5 and distillation immediately before use. The siloxycyclopropanes and benzoyl chloride were redistilled and stored in an ampule at −30 °C. Benzoylpalladium chloride complexes,[47] $Pd(Ph_3P)_4$,[48] and Pd_2(dibenzylideneacetone)$_3$·$CHCl_3$[49] were prepared as described in the following text according to a procedure reported for the preparation of related compounds.

Chlorobenzoylbis(triphenylphosphine)palladium–methylene Chloride (9). To a 40-mL benzene solution of $Pd(Ph_3P)_4$ (1.1 g, 0.96 mmol) was added benzoyl chloride (200 μL, 1.7 mmol). After 2 h at room temperature, benzene was removed in vacuo and the residue was washed five times with 5 mL each of hexane. Recrystallization from CH_2Cl_2/hexane have the title complex as yellow powder (0.73 g). Elemental analysis and ^1H NMR analysis indicated inclusion of one molecule of CH_2Cl_2 in the complex: mp 124–5 °C dec; IR (Nujol) 1659. Anal. ($C_{44}H_{37}OCl_3P_2Pd$) C, H.

Chlorobenzoylbis(triphenyl phosphite)palladium (21). To a 2-mL toluene solution of Pd_2(dibenzylideneacetone)$_3$·$CHCl_3$ (103 mg, 0.087 mmol) was added triphenyl phosphite (343 μL, 1.31 mmol). Within a few minutes, the color of the solution changed from red-purple to yellow. After 15 min, toluene was removed in vacuo, and the residue was washed seven times with 5 mL each of hexane. Gray powder was dissolved in 2.5 mL of toluene, and benzoyl chloride (80.5 μL, 0.69 mmol) was added. After the solution was heated at 60 °C for 2 h, toluene was removed in vacuo and the residue was washed five times with 4 mL each of hexane. Recrystallization from CH_2Cl_2/hexane gave the title complex as a silver-gray powder (72 mg, 48%): IR (Nujol) 1675. Anal. ($C_{43}H_{35}ClO_7P_2Pd$) C, H.

Chlorobenzoylbis(trimethylphosphine)palladium (10). To a solution of chlorobenzoylbis(triphenylphosphine)palladium (9) (524 mg, 0.613 mmol) in 5 mL of CH_2Cl_2 was added at −40 °C a 2.3 M toluene solution of trimethylphosphine (0.54 mL, 1.24 mmol), and the mixture was gradually warmed to room temperature. After 2 h, the solvent was removed in vacuo and the residue was washed repeatedly with pentane. Recrystallization twice from CH_2Cl_2/hexane gave the title compound as powder: IR (Nujol) 1637; ^1H NMR ($CDCl_3$) 1.27 (t, 18 H), 7.43–7.51 (m, 3 H), 8.10–8.17 (m, 2 H). Anal. ($C_{13}H_{23}ClOP_2Pd$) C, H.

Palladium-Catalyzed Preparation of 1,4-Keto Esters: Isopropyl 4-Phenyl-4-oxobutanoate from 5b. A solution of 1-(*tert*-butyldimethylsiloxy)-1-isopropoxycyclopropane (**5b**; 79.1 μL, 0.3 mmol), benzoyl chloride (34.8 μL, 0.3 mmol), and (PhCO)PdCl$(Ph_3P)_2$·(CH_2Cl_2) (**9**; 11.6 mg, 0.013 mmol) in 0.5 mL of strictly dry $CDCl_3$ was degassed and sealed in a test tube. After being heated at 90 °C for 14 h, the reaction mixture was concentrated and the residue was purified on silica gel (10% ethyl acetate in hexane) to obtain the title compound (64 mg, 97%): IR (neat) 2975, 2925, 1730, 1690, 1600, 1220, 1180; ^1H NMR ($CDCl_3$, 200 MHz) 1.27 (d, J = 6.3 Hz, 6 H), 2.74 (t, J = 6.7 Hz, 2 H), 3.31 (t, J = 6.7 Hz, 2 H), 5.04 (qq, J = 6.3, 6.3 Hz, 1 H), 7.43–7.64 (m, 3 H), 7.97–8.04 (m, 2 H). Anal. ($C_{13}H_{16}O_3$) C, H.

Ethyl 4-Phenyl-4-oxobutanoate from 4a. A solution of 1-ethoxy-1-(trimethylsiloxy)cyclopropane (**4a**; 959 mg, 5.5 mmol), benzoyl chloride (703 mg, 5 mmol) and $PdCl_2(Ph_3P)_2$ (35 mg, 0.05 mmol) in 2.5 mL of dry $CHCl_3$ was degassed and heated in a sealed tube at 90 °C for 15 h. The reaction mixture was concentrated, and the residue was purified on silica gel (10–15% AcOEt/hexane) to obtain the title compound (729 mg, 71%), which was identical with an authentic sample.[6a]

Examples lested in Table VII were carried out under essentially the same conditions.

Platinum-Catalyzed Preparation of 1,4-Keto Esters: Ethyl 4-Oxohexanoate. A solution of 1-ethoxy-1-(trimethylsiloxy)-cyclopropane (**4a**, 2.14 g, 11 mmol), propanoyl chloride (0.82 g, 10 mmol), and $PtCl_2(PPh_3)_2$ (**14**; 78 mg, 0.1 mmol) in 5 mL of dry $CHCl_3$ in a degassed sealed tube was heated at 90 °C for 24 h, and the reaction mixture was distilled to obtain ethyl 4-oxohexanoate (1.08 g, 68% yield): IR (neat) 2980, 2940, 2910, 1730; ^1H NMR ($CDCl_3$, 200 MHz) 1.06 (t, J = 7.6 Hz, 3 H), 1.25 (t, J = 6.7 Hz, 3 H), 2.50 (q, J = 7.6 Hz, 2 H), 2.58 (m, 2 H), 2.72 (m, 2 H), 4.12 (q, J = 6.7 Hz, 2 H). Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.30; H, 8.74.

1-(*tert*-Butyldimethylsiloxy)-1-ethoxy-2-(4-methoxyphenyl)cyclopropane (15a). To a THF (18-mL) solution of diisopropylamine (1.40 mL, 10.5 mmol) at −40 °C was added a

(45) Aoki, S.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1988**, *29*, 1541. See also: Aoki, S.; Nakamura, E. *Synlett*, in press.
(46) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(47) Cf. Fitton, P.; Johnson, M. P.; McKeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 6.
(48) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(49) Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253.

1.75 M hexane solution of *n*-butyllithium (5.75 mL, 10.0 mmol), then at −70 °C 1.40 mL of ethyl (4-methoxyphenyl)acetate (7.9 mmol), and finally after 8 min an HMPA/THF (4.8 mL/2.0 mL) solution of *tert*-butyldimethylsilyl chloride (1.53 g, 10.0 mmol) during 3 min. The reaction mixture was gradually warmed to room temperature. Hexane (70 mL) was added, and the mixture was washed several times with water and once with brine, dried over Na_2SO_4, and concentrated to obtain 2.7 g of the desired ketene acetal. To an ethereal solution (35 mL) of the crude ketene acetal was added under nitrogen a 4 M hexane solution of Et_2Zn (5 mL, 20 mmol) followed by CH_2I_2 (1.61 mL, 20.0 mmol). After 2 h, 50 mL of hexane was added. Gaseous ammonia was bubbled in, and the precipitate was removed by filtration through a pad of silica gel. Distillation of the crude product (2.6 g) gave 1.72 g (68%) of the title cyclopropane as a mixture of stereoisomers. This material contained inseparable impurities and was used as such for the experiments: bp 150–170 °C (1.2–1.3 mmHg); IR (neat) 2955, 1520, 1253, 1185, 1085, 840, 782; ^{1}H NMR 0.08, 0.19 (s, 6 H), 0.73, 0.91 (s, 9 H), 0.99, 1.22 (t, 3 H, J = 7.1 Hz), 1.05–1.52 (m, 2 H), 2.23 (dd, J = 7.2, 10.1 Hz, 1 H), 3.19–3.33, 3.57–3.70 (m, 2 H), 3.77 (s, 3 H), 6.81 (dd, J = 2.9, 8.5 Hz, 2 H), 7.10 (d, J = 8.5 Hz, 2 H).

1-(*tert*-Butyldimethylsiloxy)-1-ethoxy-2-(4-chlorophenyl)cyclopropane (15c): IR (neat) 2950, 2930, 2855, 1498, 1285, 1268, 1220, 1190, 1020, 980, 837, 780; ^{1}H NMR ($CDCl_3$) 0.09, 0.17 (s, 6 H), 0.74, 0.91 (s, 9 H), 1.00, 1.21 (t, J = 7.0 Hz, 3 H), 2.53 (dd, J = 7.1, 10.5 Hz, 1 H), 3.14–3.34, 3.57–3.61, 3.74–3.89 (m, 2 H), 7.10 (d, J = 9.1 Hz, 2 H), 7.23 (d, J = 9.1 Hz, 2 H). Anal. ($C_{17}H_{27}O_2ClSi$) C, H.

Pd/(PhO)$_3$P-Catalyzed Benzoylation of 2-Aryl-1-alkoxy-1-siloxycyclopropanes 15. A solution of the siloxycyclopropane **15** (0.20 mmol), benzoyl chloride (23.2 μL, 0.20 mmol), [PdCl(η^3-C_3H_5)]$_2$[32] (8; 3.7 mg, 0.010 mmol), and $(PhO)_3P$ (10.5 μL, 0.040 mmol) in 0.60 mL of $CHCl_3$ was degassed, sealed under vacuum, and heated at 100 °C for 9 h. The isomeric ratio was determined by GLC analysis of the crude product.

Reaction of 15a. Isolated yield, 49%; GLC retention times (OV-17, 248 °C) for 2-(4-methoxyphenyl)butanoate and its 3-aryl isomer (33:67) are 15.3 and 13.3 min, respectively. **Ethyl 2-(4-methoxyphenyl)-4-phenyl-4-oxobutanoate**: IR (neat) 2980, 2935, 2905, 1730, 1687, 1515, 1450, 1300, 1250 (br), 1180, 1160, 1035, 760, 695; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.22 (t, J = 7.1 Hz, 3 H), 3.24 (dd, J = 4.0, 17.7 Hz, 1 H), 3.80 (s, 3 H), 3.90 (dd, J = 12.0, 17.7 Hz, 1 H), 4.06–4.29 (m, 3 H), 6.88 (distorted d, J = 9.1 Hz, 2 H), 7.29 (distorted d, J = 9.1 Hz, 2 H), 7.40–7.63 (m, 3 H), 7.94–8.03 (m, 2 H). Anal. ($C_{19}H_{20}O_4$) C, H. **Ethyl 3-(4-methoxyphenyl)-4-phenyl-4-oxobutanoate**: IR (neat) 2980, 2930, 1733, 1683, 1610, 1515, 1415, 1302, 1255 (br), 1180 (br), 1035, 760, 697; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.20 (t, J = 7.2 Hz, 3 H), 2.69 (dd, J = 5.5, 17.1 Hz, 1 H), 3.33 (dd, J = 9.5, 17.1 Hz, 1 H), 3.75 (s, 3 H), 4.10 (q, J = 7.2 Hz, 2 H), 5.04 (dd, J = 5.5, 9.5 Hz, 1 H), 6.82 (distorted d, J = 8.6 Hz, 2 H), 7.18 (distorted d, J = 8.6 Hz, 2 H), 7.34–7.54 (m, 3 H), 7.94–8.03 (m, 2 H).

Reaction of 15b. Isolated yield, 62%; GLC retention times (OV-17, 245 °C) for 2-phenylbutanoate and its 3-phenyl isomer (32:68) are 8.2 and 7.4 min, respectively. **Ethyl 2,4-diphenyl-4-oxobutanoate**: IR (neat) 2985, 2930, 1737, 1692, 1227, 1165, 760, 700; ^{1}H NMR 1.21 (t, J = 7.2 Hz, 3 H), 3.26 (dd, J = 4.0, 18.2 Hz, 1 H), 3.95 (dd, J = 10.7, 18.2 Hz, 1 H), 4.0–4.2 (m, 3 H), 4.27 (dd, J = 4.0, 10.7 Hz, 1 H), 7.25–7.60 (m, 8 H), 7.98 (distorted d, J = 8 Hz, 2 H). **Ethyl 3,4-diphenyl-4-oxobutanoate**: IR (neat) 2975, 2925, 1737, 1685, 1235, 1180, 760, 700; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.22 (t, J = 7.2 Hz, 3 H), 2.71 (dd, J = 5.3, 17.1 Hz, 1 H), 3.36 (dd, J = 9.7, 17.1 Hz, 1 H), 4.10 (q, J = 7.2 Hz, 2 H), 5.08 (dd, J = 5.3, 9.7 Hz, 1 H), 7.2–7.5 (m, 8 H), 7.96 (distorted d, J = 8.2 Hz, 2 H).

Reaction of 15c. Isolated yield, 55%; GLC retention times (OV-17, 225 °C) for 2-phenylbutanoate and its 3-phenyl isomer (22:78) are 21.5 and 18.3 min, respectively. **Ethyl 2-(4-chlorophenyl)-4-phenyl-4-oxobutanoate**: IR (neat) 2980, 1733, 1687, 1493, 1160, 1095, 1020, 760, 693; ^{1}H NMR 1.21 (t, J = 7.2 Hz, 3 H), 3.26 (dd, J = 4.2, 18.0 Hz, 1 H), 3.90 (dd, J = 10.3, 18.0 Hz, 1 H), 4.06–4.20 (m, 2 H), 7.31 (s, 4 H), 7.40–7.63 (m, 3 H), 7.93–8.01 (m, 2 H). Anal. ($C_{18}H_{17}O_3Cl$) C, H. **Ethyl 3-(4-chlorophenyl)-4-phenyl-4-oxobutanoate**: IR (neat) 2980, 1733, 1685, 1493, 1235, 1095 (br, sh), 1180 (br), 1095; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.19 (t, J = 7.1 Hz, 3 H), 2.69 (dd, J = 5.5, 17.0 Hz, 1 H), 3.33 (dd, J = 9.9, 17.0 Hz, 1 H), 4.10 (q, J = 7.1 Hz, 2 H), 5.06 (dd, J = 5.5, 9.9 Hz, 1 H), 7.20–7.29 (m, 4 H), 7.31–7.54 (m, 3 H), 7.90–7.97 (m, 2 H). Anal. ($C_{18}H_{17}O_3Cl$) C, H.

Benzoylation of 5b in the Presence of Chlorobenzoylbis(trimethylphosphine)palladium (10). The acylation reaction with the catalyst having Me_3P as a ligand was carried out as usual in an NMR tube to obtain the keto ester **12** (27%) and the hydrolytically unstable ketene acetal **13** (33%) (Scheme II). The latter compound consisted of a single stereoisomer that gave **13** upon hydrolysis and showed the following spectral properties: ^{1}H NMR ($CDCl_3$, 200 MHz) 2.71 (dd, J = 2.5, 17.0 Hz, 1 H, PhCOCH), 2.82 (dd, J = 3.0, 17.0 Hz, 1 H, PhCOCH), 4.26 (qq, J = 6.2, 6.2 Hz, OCH), 5.29 (dd, J = 2.5, 3.0 Hz, 1 H, CH=, coupled to the signals at 2.71 and 2.82); MS (EI) 277 (2, $-C_4H_9$), 115 (21, Si-*t*-BuMe$_2$), 105 (100, PhCO), 77 (31, pH).

Physical Properties of 1,4-Keto Esters. Ethyl (4-chlorophenyl)-4-oxobutanoate: IR (CCl_4) 2980, 1738, 1695, 1590, 1550, 1215, 1175, 1095; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.28 (t, J = 7.2 Hz, 3 H), 2.77 (t, J = 6.3 Hz, 2 H), 3.30 (t, J = 6.3 Hz, 2 H), 4.18 (q, J = 7.2 Hz, 2 H), 7.48 (distorted d, J = 10 Hz, 2 H), 7.97 (distorted d, J = 10 Hz, 2 H). Anal. ($C_{12}H_{13}ClO_3$) C, H.

Ethyl (4-methoxyphenyl)-4-oxobutanoate: IR (neat) 2975, 2840, 1720, 1670, 1260, 1160; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.26 (t, J = 7.4 Hz, 3 H), 2.75 (t, J = 6.9 Hz, 2 H), 3.27 (t, J = 6.9 Hz, 2 H), 3.86 (s, 3 H), 4.16 (q, J = 7.4 Hz, 2 H), 6.97 (d, J = 9.7 Hz, 2 H), 7.98 (d, J = 9.7 Hz, 2 H). Anal. ($C_{13}H_{16}O_4$) C, H.

Ethyl 4-oxopentadecanoate: IR (neat) 2920, 2850, 1730, 1715, 1270, 1180; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.88 (t, J = 6.9 Hz, 3 H), 1.23 (m, 19 H), 1.58 (m, 2 H), 2.45 (t, J = 7.4 Hz, 2 H), 2.58 (t, J = 6.9 Hz, 2 H), 2.73 (t, J = 6.9 Hz, 2 H), 4.13 (q, J = 6.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) 14.1, 22.8, 23.9, 28.1, 30.0–30.7, 32.0, 37.1, 43.0, 60.8, 173.0, 209.3. Anal. ($C_{17}H_{32}O_3$) C, H.

Ethyl 4-oxo-6-phenylhexanoate: IR (neat) 2980, 1730, 1720, 1375, 1185; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.24 (t, J = 7.2 Hz, 3 H), 2.58 (t, J = 6.3 Hz, 2 H), 2.71 (t, J = 6.3 Hz, 2 H), 2.79 (t, J = 7.4 Hz, 2 H), 2.92 (t, J = 7.4 Hz, 2 H), 4.13 (d, J = 7.2 Hz, 2 H), 7.46–7.60 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) 14.3, 28.1, 30.0, 37.3, 44.3, 60.7, 126.1, 128.3, 128.4, 140.9 (2 peaks), 172.7, 207.8. Anal. ($C_{14}H_{18}O_3$) C, H.

Ethyl 2-methyl-4-phenyl-4-oxobutanoate: IR (neat) 2975, 2930, 1735, 1690, 1600, 1215, 1180; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.27 (t, J = 7.1 Hz, 3 H), 1.30 (d, J = 7.1 Hz, 3 H), 3.04 (dd, J = 5.6, 17.1 Hz, 1 H), 3.13 (ddq, J = 5.6, 7.1, 7.1 Hz, 1 H), 3.50 (dd, J = 7.1, 17.1 Hz, 1 H), 4.16 (q, J = 7.1 Hz, 2 H), 7.43–7.64 (m, 3 H), 7.97–8.03 (m, 2 H). Anal. ($C_{13}H_{16}O_3$) C, H.

Ethyl 2-methyl-4-(4-chlorophenyl)-4-oxobutanoate: IR (neat) 2980, 1735, 1690, 1593, 1215, 1180; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.26 (t, J = 7.2 Hz, 3 H), 1.28 (d, J = 7.1 Hz, 3 H), 2.96 (dd, J = 5.6, 17.1 Hz, 1 H), 3.11 (ddq, J = 5.6, 7.1, 7.5 Hz, 1 H), 3.46 (dd, J = 7.5, 17.1 Hz, 1 H), 7.45 (distorted d, J = 8.9 Hz, 2 H), 7.93 (distorted d, J = 8.9 Hz, 2 H). Anal. ($C_{13}H_{15}ClO_3$) C, H.

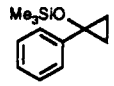
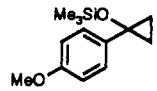
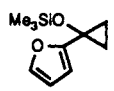
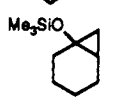
Ethyl 2-methyl-4-(4-methoxyphenyl)-4-oxobutanoate: ^{1}H NMR (CCl_4, 60 MHz) 1.0–1.4 (m, 6 H), 2.6–3.4 (m, 3 H), 3.90 (s, 3 H), 4.05 (d, J = 7 Hz, 2 H), 6.8 (distorted d, J = 9 Hz, 2 H), 7.8 (distorted d, J = 9 Hz, 2 H).

Ethyl 2-methyl-4-oxopentadecanoate: IR (neat) 2920, 2850, 1725, 1720, 1465, 1180, 1140; ^{1}H NMR (CCl_4, 60 MHz) 0.7–1.8 (m, 27 H), 2.0–2.9 (m, 5 H), 4.0 (d, J = 7 Hz, 2 H). Anal. ($C_{18}H_{30}O_3$) C, H.

Ethyl 2-methyl-4-oxo-6-phenylhexanoate: IR (neat) 2975, 2930, 1733, 1720, 1185, 1150; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.16 (d, J = 7.1 Hz, 3 H), 1.25 (t, J = 7.1 Hz, 3 H), 2.34–2.51 (m, 1 H), 2.71–3.00 (m, 6 H), 7.14–7.37 (m, 5 H). Anal. ($C_{15}H_{20}O_3$) C, H.

Palladium-Catalyzed Preparation of 1,4-Diketones: 1-(4-Methoxyphenyl)-4-(2-methylphenyl)butane-1,4-dione. A solution of 1-(trimethylsiloxy)-1-(4-methoxyphenyl)cyclopropane (92.6 μL, 0.4 mmol), 2-methylbenzoyl chloride (26.1 μL, 0.2 mmol), [(η^3-C_3H_5)PdCl]$_2$ (18; 1.8 mg, 0.005 mmol), and triphenyl phosphite (5.4 μL, 0.02 mmol) in 0.8 mL of HMPA was heated at 100 °C for 20 h under CO pressure (10 atm) to obtain the desired 1,4-diketone (43.7 mg, 77%) after flash column chromatography: IR ($CHCl_3$) 1680, 1605, 1580, 1515, 1265, 1255, 1235, 1175; ^{1}H NMR ($CDCl_3$, 200 MHz) 2.51 (s, 3 H), 3.20–3.50 (m, 4 H), 3.89 (s, 3 H),

Table VIII. Preparation of 1,4-Diketones under 10 atm of CO Pressure at 100 °C for 20 h in HMPA[a]

cyclopropane		acid chloride				
	μL, mmol		μL, mmol	catalyst	conditions (°C, h)	yield (mg, %)
	64, 0.30	1-$C_{10}H_7COCl$	30.1, 0.20	A	100, 20	53[b]
 19	92.6, 0.40	1-$C_{10}H_7COCl$	30.1, 0.20	B	100, 20	60, 69
	92.6, 0.40	C_6H_5COCl	23.2, 0.20	B	100, 20	44, 75
	92.6, 0.40	o-$CH_3C_6H_4COCl$	26.1, 0.20	B	100, 20	44, 77
	92.6, 0.40	p-ClC_6H_5COCl	25.4, 0.20	B	100, 20	40, 55
	81.8, 0.40	m-MeC_6H_4COCl	40, 0.20	B	100, 20	25, 52
	81. 0.40	1-$C_{10}H_7COCl$	30.1, 0.20	B	100, 20	21, 46
	81, 0.40	2-thenoyl chloride	21.4, 0.20	C	70, 24	21, 46
	101, 0.40	2-thenoyl chloride	21.4, 0.20	D	70, 24	24, 56

[a] Catalyst A: 8 (7.0 mg, 10 μmol). Catalyst B: 18 (1.8 mg, 5 μmol) + $(PhO)_3P$ (5.4 μL, 20 μmol). Cataly 18 (3.0 mg, 8.3 μmol) + $(PhO)_3P$ (9 μL, 33 μmol). Catalyst D: 18 (2.2 mg, 6.1 μmol) + $(PhO)_3P$ (6.6 μL, 24 μmol). [b] Calculated from ii letely purified product.

Table IX. Kinetic Analysis of the Aroylation of Siloxycyclopropanes with XC_6H_4COCl in the Presence of Palladium Catalysts (9.0 mol %)

cyclopropane	X	catalyst	$k^2 \times 10^2$ ($M^{-0.44}$ min^{-1})
5b	H	$PhCOPdCl(Ph_3P)_2 \cdot CH_2Cl_2$ (**9**)	9.3
4b	H	$PhCOPdCl(Ph_3P)_2 \cdot CH_2Cl_2$ (**9**)	7.1
6	H	$PhCOPdCl(Ph_3P)_2 \cdot CH_2Cl_2$ (**9**)	1.3
5b	H	$PhCOPdCl(PhO_3P)_2$ (**21**)	47
5b	H	$PhCOPdCl(Me_3P)_2$ (**10**)	1.9
5b	m-NO_2	$PhCOPdCl(Ph_3P)_2 \cdot CH_2Cl_2$ (**9**)	9.9
5b	p-Cl	$PhCOPdCl(Ph_3P)_2 \cdot CH_2Cl_2$ (**9**)	7.9
5b	p-CH_3	$PhCOPdCl(Ph_3P)_2 \cdot CH_2Cl_2$ (**9**)	9.7
5b	p-OCH_3	$PhCOPdCl(Ph_3P)_2 \cdot CH_2Cl_2$ (**9**)	7.2

6.97 (distorted d, J = 8.6 Hz, 2 H), 7.10–7.50 (m, 3 H), 7.86 (distorted d, J = 7.6 Hz, 1 H), 8.03 (distorted d, J = 8.6 Hz, 2 H). Anal. ($C_{18}H_{18}O_3$) C, H.

Physical Properties of 1,4-Diketones. 1-Naphthyl-4-phenylbutane-1,4-dione: IR ($CHCl_3$) 1685, 1595, 1235, 1105; ^1H NMR ($CDCl_3$, 200 MHz) 3.55 (m, 4 H), 7.3–7.7 (m, 6 H), 7.8–8.2 (m, 5 H), 8.6 (m, 1 H). Anal. ($C_{20}H_{16}O_2$) C, H.

1-(4-Methoxyphenyl)-4-naphthylbutane-1,4-dione: IR ($CHCl_3$) 1680, 1605, 1580, 1515, 1265, 1255, 1240, 1175; ^1H NMR ($CDCl_3$, 200 MHz) 3.50 (s, 4 H), 3.88 (s, 3 H), 6.98 (distorted d, J = 8.9 Hz, 2 H), 7.45–7.66 (m, 3 H), 7.83–7.93 (m, 1 H), 7.93–8.15 (m, 4 H), 8.61 (m, 1 H). Anal. ($C_{21}H_{18}O_3$) C, H.

1-(4-Methoxyphenyl)-4-phenylbutane-1,4-dione: IR ($CHCl_3$) 1680, 1605, 1580, 1515, 1265, 1235, 1175; ^1H NMR ($CDCl_3$, 200 MHz) 3.44 (m, 4 H), 3.88 (s, 3 H), 6.95 (distorted d, J = 8.9 Hz, 2 H), 7.40–7.65 (m, 3 H), 7.96–8.12 (m, 4 H). Anal. ($C_{17}H_{16}O_3$) C, H.

1-(4-Chlorophenyl)-4-(4-methoxyphenyl)butane-1,4-dione: IR ($CHCl_3$) 1680, 1605, 1580, 1515, 1405, 1265, 1235, 1175; ^1H NMR ($CDCl_3$, 200 MHz) 3.42 (br s, 4 H), 3.88 (s, 3 H), 6.98 (distorted d, J = 8.9 Hz, 2 H), 7.47 (distorted d, J = 8.6 Hz, 2 H), 8.00 (distorted d, J = 8.6 Hz, 2 H), 8.05 (distorted d, J = 8.9 Hz, 2 H). Anal. ($C_{17}H_{15}ClO_3$) C, H.

1-(2-Furyl)-4-(3-methylphenyl)butane-1,4-dione: IR ($CHCl_3$) 1680, 1605, 1590, 1575, 1475, 1400, 1255, 1160; ^1H NMR ($CDCl_3$, 200 MHz) 2.43 (s, 3 H), 3.31 (m, 2 H), 3.46 (m, 2 H), 6.57 (m, 1 H), 7.30 (m, 1 H), 7.40 (br s, 2 H), 7.66 (br s, 1 H), 7.86 (br s, 2 H). Anal. ($C_{15}H_{14}O_3$) C, H.

2-(2-(1-Naphthyl)-2-oxoethyl)cyclohexanone: IR ($CHCl_3$) 2940, 1710, 1685; ^1H NMR ($CDCl_3$, 200 MHz) 1.40–2.05 (m, 4 H), 2.05–2.33 (m, 2 H), 2.33–2.65 (m, 2 H), 2.75 (dd, J = 5.1, 17.1 Hz, 1 H), 3.27 (m, 1 H), 3.52 (dd, J = 7.6, 17.1 Hz, 1 H), 7.35–7.65 (m, 3 H), 7.75–8.05 (m, 3 H), 8.52 (m, 1 H). Anal. ($C_{18}H_{18}O_2$) C, H.

2-(2-(2-Thienyl)-2-oxoethyl)cyclanone: ^1H NMR ($CDCl_3$, 200 MHz) 1.0–2.5 (m, 8 H), 2.66 (dd, J = 6.8, 11.4 Hz, 1 H), 3.11 (tt, J = 6.8, 6.8 Hz, 1 H), 3.51 (dd, J = 6.8, 11.4 Hz, 1 H), 7.14 (dd, J = 4.6, 5.7 Hz, 1 H), 7.64 (d, J = 5.7 Hz, 1 H), 7.80 (d, J = 4.6 Hz, 1 H). Anal. ($C_{12}H_{14}O_2S$) C, H, S.

1-(2-Thienyl)-3-methylhexane-1,4-dione: ^1H NMR ($CDCl_3$, 200 MHz) 1.07 (t, J = 6.7 Hz, 3 H), 1.17 (d, J = 6.7 Hz, 3 H), 2.64 (q, J = 6.7 Hz, 2 H), 2.90 (dd, J = 4.8, 17.1 Hz, 1 H), 3.22 (m, 1 H), 3.48 (dd, J = 8.6, 17.1 Hz, 1 H), 7.11 (dd, J = 3.8, 4.8 Hz, 1 H), 7.62 (dd, J = 1.1, 4.8 Hz, 1 H), 7.73 (dd, J = 1.1, 3.8 Hz, 1 H). Anal. ($C_{11}H_{14}O_2S$) C, H, S.

Kinetic Studies of the Acylation Reaction. For kinetic studies, solvent and starting materials were redistilled or recrystallized before use, and analytically pure samples of the palladium complexes were employed. The palladium complexes are used as a stock solution in $CDCl_3$.

General Procedure for the Kinetic Experiments. To an oven-dried 5-mm o.d. NMR sample tube were taken the required amounts of a siloxycyclopropane (e.g., **5b**, 79.5 μL, 0.30 mmol), benzoyl chloride (e.g., 34.8 μL, 0.30 mmol), and the stock solution of a palladium catalyst, and the mixture was diluted with $CDCl_3$ to make a total volume of 0.50 mL. After several freeze/thaw cycles, the tube was sealed under vacuum. To maintain reproducibility of the data, samples for a series of experiments were made at the same time from a single lot of the starting materials and catalyst and were kept at −30 °C until used. The purity of the palladium catalyst was especially crucial for the reproducibility. The sample tube was inserted to the NMR probe preheated to 90 °C, and the progress of the reaction was determined by integration of the area of isopropyl methyne protons of the siloxycyclopropane and the keto ester as well as that of the C_2 and C_3 methylene protons of the keto ester. The kinetic data are summarized in Table IX.

Acknowledgment. We thank the Asahi Glass Foundation for financial support, Dr. Andrea Dorigo for helpful suggestions in theoretical calculations, and Dr. P. G. Williard for searching the crystallographic data base. Theoretical calculations have been carried out on HITAC S-820/80 computer at the Computer Center, the Institute for Molecular Science, Okazaki National Research Institutes.

Registry No. **1**, 75-19-4; **2**, 16545-68-9; **3**, 15144-65-7; **4a**, 27374-25-0; **4b**, 84098-44-2; **5a**, 117726-73-5; **5b**, 96760-01-9; **6**, 113777-08-5; **7a** (R = *i*-Pr, R^3 = C_6H_5), 104750-69-8; **7a** (R = Et, R^3 = p-ClC_6H_4), 53503-49-4; **7a** (R = Et, R^3 = CH_3CH_2), 3249-33-0; **7a** (R = Et, R^3 = C_6H_5), 6270-17-3; **7a** (R = Et, R^3 = p-$MeOC_6H_4$, 15118-67-9; **7a** (R = Et, R^3 = (*E*)-C_6H_5CH=CH), 121748-58-1; **7a** (R = Et, R^3 = $CH_3(CH_2)_{10}$), 93479-77-7; **7a** (R = Et, R^3 =

$C_6H_5(CH_2)_2$), 90147-73-2; **7a** (R = *i*-Pr, R^3 = $C_6H_5(CH_2)_2$), 127931-46-8; **7b** (R = Et, R^3 = *p*-ClC_6H_4), 40394-88-5; **7b** (R = Et, R^3 *p*-$MeOC_6H_4$), 132566-33-7; **7b** (R = Et, R^3 = $CH_3(CH_2)_{10}$), 132566-34-8; **7b** (R = Et, R^3 = $C_6H_5(CH_2)_2$), 132566-35-9; **7b** (R = Et, R^3 = C_6H_5), 40394-84-1; **8**, 13965-03-2; **9**, 132566-21-3; **10**, 68391-84-4; **12**, 104750-69-8; **13**, 132566-32-6; **14**, 10199-34-5; *cis*-**15a**, 132566-24-6; *trans*-**15a**, 132566-36-0; **15b**, 132566-25-7; **15c**, 132566-26-8; **16a**, 132566-27-9; **16b**, 132566-29-1; **16c**, 132566-30-4; **17a**, 132566-28-0; **17b**, 53647-50-0; **17c**, 132566-31-5; **18**, 12012-95-2; **19**, 60068-19-1; **20**, 127931-49-1; **21**, 41798-91-8; C_6H_5COCl, 98-88-4; $(C_6H_5CO)_2O$, 93-97-0; C_6H_5COBr, 618-32-6; *p*-ClC_6H_4COCl, 122-01-0; *p*-$MeOC_6H_4COCl$, 100-07-2; (*E*)-C_6H_5CH=$CHCOCl$, 17082-09-6; $CH_3(CH_2)_{10}COCl$, 112-16-3; $C_6H_5(CH_2)_2COCl$, 645-45-4; CH_3CH_2COCl, 79-03-8; 1-$C_{10}H_7COCl$, 879-18-5; 2-MeC_6H_4COCl, 933-88-0; 3-MeC_6H_4COCl, 1711-06-4; $(CH_3)_2C$=$CHCOCl$, 3350-78-5; $C_6H_5CO(CH_2)_2COC_{10}H_7$-1, 127931-48-0; *p*-$MeOC_6H_4CO(CH_2)_2COC_6H_5$, 60755-22-8; *p*-$MeOC_6H_4CO(CH_2)_2COC_6H_4$-*o*-Me, 127931-50-4; *p*-$MeOC_6H_4CO$-$(CH_2)_2COC_6H_4$-*p*-Cl, 67756-16-5; $CH_3CH_2COCH(CH_3)CH_2CO$-C_6H_5, 121862-34-8; $PdCl_2$, 7047-10-1; $PdCl_2$(*o*-$Tol_3P)_2$, 40691-33-6; $Pd(Ph_3P)_4$, 14221-01-3; $Pd_2(dba)_3$·$CHCl_3$, 52522-40-4; *p*-$MeOC_6H_4CH_2COOEt$, 14062-18-1; 1-((trimethylsilyl)oxy)-1-phenylcyclopropane, 38858-73-0; 1-((trimethylsilyl)oxy)-1-(2-furyl)cyclopropane, 132566-22-4; 1-((trimethylsilyl)oxy)bicyclo-[4.1.0]heptane, 38858-74-1; 2-thenoyl chloride, 5271-67-0; 1-(2-furyl)-4-(3-methylphenyl)butane-1,4-dione, 127931-51-5; 2-[2-(1-naphthyl)-2-oxoethyl]cyclohexanone, 127931-52-6; 2-[2-(2-thienyl)-2-oxoethyl]cyclohexanone, 54669-95-3; 1-(2-thienyl)-3-methylhexane-1,4-dione, 132566-23-5; 1-((trimethylsilyl)oxy)-1-ethyl-2-methylcyclopropane, 113777-09-6.

Structural Requirements for Glyme Catalysis in Butylaminolysis of Aryl Acetates in Chlorobenzene. Identification of $-OCH_2CH_2OCH_2CH_2OCH_2CH_2O-$ as the Optimal Subunit for Catalysis

John C. Hogan and Richard D. Gandour*

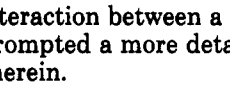
Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804

Received September 25, 1990

The catalytic behavior of linear (open-chain) polyethers (glymes) in butylaminolysis of 4-nitrophenyl acetate carried out in chlorobenzene has been reexamined (*J. Am. Chem. Soc.* **1980**, *102*, 2865–2866). The observation of a break in a plot of the catalytic rate constant vs chain length of catalyst indicates that four oxygens in a $-OCH_2CH_2OCH_2CH_2OCH_2CH_2O-$ subunit are necessary for optimal catalysis. The break, occurring at four oxygens in the profile (corresponds to triglyme), has been verified by a Hammett analysis, which employed four additional aryl acetates (3-chlorophenyl, 3-bromophenyl, 3-cyanophenyl, and 4-cyanophenyl). This break was missed in a previous study (*J. Am. Chem. Soc.* **1980**, *102*, 2865–2866) because differing amounts of impurities in the glymes increased the experimental scatter of the data. The Hammett study supports the conclusions of others that breakdown of the zwitterionic tetrahedral intermediate is rate-limiting. The break in the polyether plot implies a specific structure for a glyme–zwitterionic tetrahedral intermediate complex, which contains an ammonium ion that hydrogen bonds to the ether oxygens.

Introduction

In 1980, we demonstrated[1] that conformational flexibility enhances the catalytic power of glymes in the butylaminolysis of 4-nitrophenyl acetate conducted in chlorobenzene. We showed that glyme catalysis of this reaction exhibits an *inverse macrocyclic effect*;[2] i.e., open-chain polyethers, GLM(*n*), are better catalysts than macrocyclic polyethers. Our desire to understand the mechanism of this host–guest interaction between a catalyst and transition structure prompted a more detailed examination, which we report herein.



GLM(n)

Ester aminolysis carried out in nonpolar media[3–5] proceeds via the rate-determining breakdown of a tetrahedral intermediate, $T^{\pm}$. The rate expression, eq 1, indicates a termolecular transition structure. Base catalysis of the

$$k_{obs} = k_0[\text{amine}]^2 + k_{cat}[\text{amine}][\text{catalyst}] \quad (1)$$

reaction involves[5–7] a hydrogen-bonded complex, presumably between the catalyst and the ammonium ion part of $T^{\pm}$. Scheme I illustrates a minimal mechanism. Formation of the catalyst·$T^{\pm}$ complex can occur by two paths. Breakdown of the complex most likely limits the rate.

Glyme catalysis of this aminolysis improves[1] as the number of basic oxygen atoms per catalyst molecule increases, which is the expected behavior if complexation assists in the rate-determining breakdown of $T^{\pm}$. Complexation by polyether bases to an acidic site (i.e., the ammonium region of $T^{\pm}$) should improve with the number

Table I. Melting and Boiling Points of Aryl Acetates

substituent	mp or bp (Torr), °C	lit. bp (Torr) or mp, °C	lit. ref
3-chloro	70.5 (2)	105–109 (15–16)	8
3-bromo	86.5 (2)	142 (34)	9
3-cyano	60.0–60.5	58	9
4-cyano	57.0–58.0	56–57	8
4-nitro	78.0–79.5	79	9

(1) Hogan, J. C.; Gandour, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 2865–2866.
(2) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540–6541.
(3) Menger, F. M.; Smith, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 3824–3829.
(4) Menger, F. M.; Vitale, A. C. *J. Am. Chem. Soc.* **1973**, *95*, 4931–4934.
(5) Nagy, O. B.; Reuliaux, V.; Bertrand, N.; Van Der Mensbrugghe, A.; Leseul, J.; Nagy, J. B. *Bull. Soc. Chim. Belg.* **1985**, *94*, 1055–1074.
(6) Su, C.-W.; Watson, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 1854–1857.
(7) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511–527.

0022-3263/91/1956-2821$02.50/0