On an (Oxatrimethylenemethane)palladium(0) Complex. An Unusual Palladium(0)-Catalyzed Cyclopropanation

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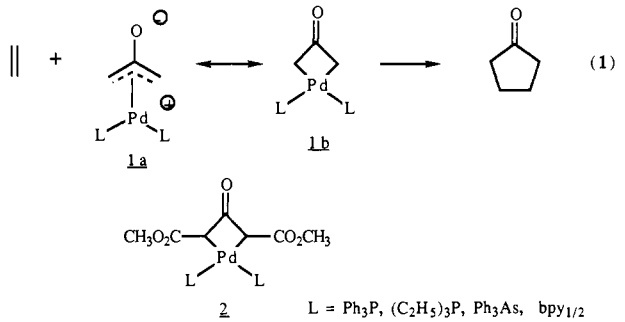
Abstract: A study of the cycloadditions invoking (oxatrimethylenemethane)palladium as a transient intermediate in a catalytic cycle contrasts with the all-carbon system in giving rise to a net [2 + 1] cycloaddition with electron-rich strained olefins rather than the [2 + 3] cycloaddition of the carbon analogue with electron-deficient olefins. The bifunctional conjunctive reagents 1-(acyloxy)-3-silyl-2-propanones are formed by the reaction of the appropriate glycolic acid derivative with a (silylmethyl)-magnesium chloride. Pd(0) complexes catalyze diastereocontrolled cyclopropanation of norbornenes with these substrates in good yields. No [3 + 2] cycloadducts are observed. The unexpected cyclopropanation in lieu of cyclopentanone annulation is rationalized in terms of the bonding of the (oxatrimethylenemethane)palladium complex.

The development of cycloaddition reactions catalyzed by Pd(0) has mainly involved the equivalent of the transfer of a trimethylenemethane fragment.[1-5] The development of the oxygen analogue could provide a direct synthesis of cyclopentanones according to eq 1.[6] In this regard, it is interesting to note that



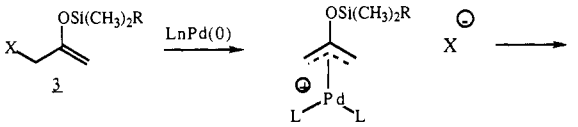
(1)

the palladacyclobutanone **2** is a readily available stable complex.[7] Unfortunately, in our hands, it does not show any signs of participating in cycloadditions. On the supposition that the ester groups too strongly stabilized the proposed "reactive" intermediate, we examined the in situ generation of the parent 3-palladacyclobutanone **1**. In this paper, we report our efforts toward the generation of **1** and its participation in cycloadditions which contrasts sharply with the all-carbon analogue.

Table I. Preparation α-(Acyloxy)-α′-silylacetone

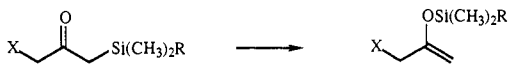
entry	X	Y	R	M	isolated yield, %
1	OAc	Cl	CH_3	MgCl	34%
2	OAc	$OCOCH_2OAc$	CH_3	MgCl	56%
3	OCO_2CH_3	Cl	CH_3	MgCl	9%
4	OCO_2CH_3	Cl	CH_3	ZnI	2%
5	OCO_2CH_3	$OCOCH_2OCO_2CH_3$	CH_3	MgCl	16%
6	OAc	$OCOCH_2OAc$	Ph	MgCl	89%

We envisioned the utilization of an oxygen analogue **3** of our bifunctional conjunctive reagent 2-(acetoxymethyl)-3-(trimethylsilyl)-1-propene according to eq 2. Based upon the work



1 + $XSi(CH_3)_2R$ (2)

of Sakurai,[8] a simple preparation of enol silyl ethers such as **3** relies upon a Brooke rearrangement (eq 3). During the course



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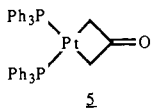
of our studies, Kemmitt et al. reported the preparation of several metallacyclobutanones including the platinum complex **5** from



3, X = Cl and R = CH_3, and that the Brooke rearrangement of eq 3 was catalyzed by tetrakis(triphenylphosphine)palladium.[9] The absence of the palladium complex from this report supported our notion that it may be more reactive and thereby participate in a catalytic cycloaddition cycle.

Preparation of Bifunctional Conjunctive Reagents. In a procedure analogous to the preparation of the chloride **4**, we prepared the acetoxy (**4**, X = OAc, R = CH_3 and Ph) and methoxycarboxy

(1) For a review, see Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.

(2) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315, 2326. Trost, B. M.; Bonk, P. J. *Ibid.* **1985**, *107*, 8277. Trost, B. M.; Seone, P. R. *Ibid.* **1987**, *109*, 615. Trost, B. M.; MacPherson, D. T. *Ibid.* **1987**, *109*, 3483.

(3) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 5183.

(4) Binger, P.; Schuchardt, U. *Chem. Ber.* **1980**, *113*, 3334; **1981**, *114*, 3313.

(5) Also see Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1985**, *26*, 3825.

(6) For additions of α,α′-dihalo ketones with olefins and dienes, see: Noyori, R.; Makino, S.; Takayo, H. *J. Am. Chem. Soc.* **1971**, *93*, 1272. Chidgey, R.; Hoffmann, H. M. R. *Tetrahedron Lett.* **1977**, 2633. Mann, J.; Overton, H. J.; Lewis, T. *Tetrahedron Lett.* **1985**, *26*, 6133. For additions from monohalo ketones, see: Sakurai, H.; Shirahata, A.; Hosomi, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 163. Mann, J.; Usmani, A. *J. Chem. Soc., Chem. Commun.* **1980**, 1119. Cowling, A. P.; Mann, J.; Usmani, A. A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2116. Bowers, K. G.; Mann, J. *Tetrahedron Lett.* **1985**, *26*, 4411. Shimizu, N.; Tanaka, M.; Tsuno, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1330 and references cited therein. For reviews, see: Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1. Noyori, R.; Hayakawa, Y. *Org. React.* **1983**, *29*, 163.

(7) Kemmitt, R. D. W.; McKenne, P.; Russell, B. R.; Sherry, L. J. S. *J. Chem. Soc., Dalton Trans.* **1985**, 259. For a related monoester complex, *syn*-1-carboethoxy-2-hydroxy-π-allylpalladium chloride dimer, see: Yanase, N.; Nakamura, Y.; Kawaguchi, S. *Inorg. Chem.* **1980**, *19*, 1575.

(8) Sakurai, H.; Shirahata, A.; Araki, Y.; Hosomi, A. *Tetrahedron Lett.* **1980**, *21*, 2325. Hosomi, A.; Shirahata, A.; Araki, Y.; Sakurai, H. *J. Org. Chem.* **1981**, *46*, 4613.

(9) Jones, M. D.; Kemmitt, R. D. W.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1986**, 427.

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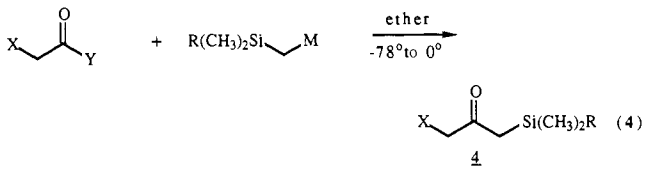
(**4**, X = OCO_2CH_3, R = CH_3) conjunctive reagents from the corresponding glycolic acid derivatives[10] according to eq 4 and Table I. The presence of two carboxylic functional groups in our substrates raises the question of the chemoselectivity of the attack on the organometallic. An inspection of the table reveals



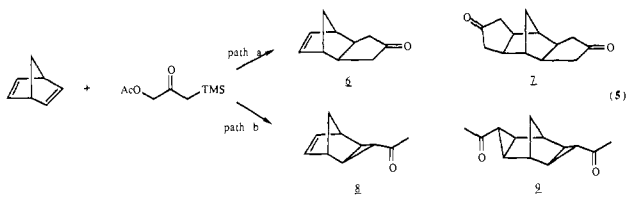
(4)

4

that satisfactory results can be obtained with the Grignard reagent and the symmetrical anhydride. Surprisingly, substantial yield improvement was observed when the dimethylphenylsilyl substituent replaced the trimethylsilyl substituent—an observation that suggests that some of the yield loss may arise by silicon migrations at intermediate stages of the acylation.

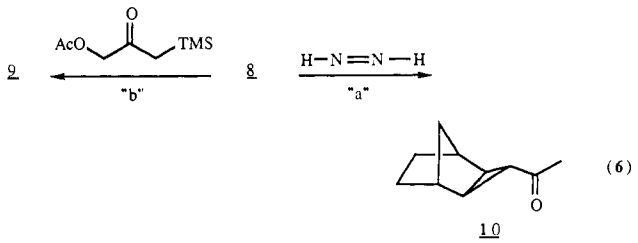
Cycloadditions. Since we intended to utilize Pd(0) to catalyze our cycloadditions and tetrakis(triphenylphosphine)palladium is reported to catalyze the Brooke rearrangement of **4** (X = Cl, R = CH_3),[9] we explored the direct utilization of our C–silyl ketones. Exposing a benzene-d_6 solution of the acetoxy ketone **4** (X = OAc, R = CH_3) to a Pd(0) catalyst prepared from $(dba)_3Pd_2{\cdot}CHCl_3$[11] and triphenylphosphine at 80 °C led to isomerization to the corresponding enol silyl ether **3** (X = OAc, R = CH_3) within 1 min as determined by NMR spectroscopy. Thus, cycloadditions to olefins were examined by treating a benzene solution of the C–silyl ketone **4** with an excess of the olefin and 5 mol % of a Pd(0) catalyst formed by disproportionating $(dba)_3Pd_2{\cdot}CHCl_3$ with triphenylphosphine (P:Pd, 4:1).

Electron-deficient olefins such as dimethyl benzylidenemalonate, which are excellent acceptors in Pd(0)-catalyzed cycloadditions with 2-(acetoxymethyl)-3-(trimethylsilyl)-1-propene,[1,2] failed to react as did simple olefins such as 1-decene or cyclohexene. On the other hand, norbornadiene led to a smooth reaction. Two



(5)

products were isolated—a monoadduct (56% yield) and a diadduct (17% yield)—which would be expected to be the mono- and dicyclopentanones **6** and **7**, respectively. The infrared spectra (1685 and 1690 cm^{-1}, respectively), however, did not support the presence of any saturated five-membered ring ketones. Most noteworthy was the presence of a 3 H singlet at δ 2.19 and a 6 H singlet at δ 2.17 in the NMR spectra of the mono- and diadducts, respectively, which are strongly indicative of methyl ketones. Confirmation of the cyclopropyl structure **8** for the monoadduct arose by its diimide reduction to the known *exo*-cyclopropyl ketone **10** (eq 6a), whose spectral properties and melting point agreed

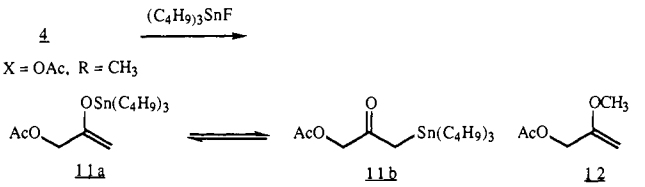


(6)

9 **8** **10**

well with those reported.[12,13] The structure of the diadduct as a biscyclopropanation product **9** rests upon (1) its high symmetry as indicated by its ^1H NMR spectrum, which shows only five types of protons in a 2:4:6:2:2 ratio (i.e., D_{2d} symmetry), and (2) its formation by the further reaction of the monoadduct **8** (eq 6b).

The unexpected cyclopropanation led us to examine the effect of cyclization on substrate and catalyst. The chloride analogue **4** (X = Cl, R = CH_3) fails to form cycloadducts. This result is most surprising in light of the facility with which this substrate is found to form metallacyclobutanones with other metals.[9] Changing the silicon substituent, i.e., from **4** where X = OAc, R = CH_3 to **4** where X = OAc, R = Ph, has no effect on the reaction. In situ formation of the stannane **11** by treating **4** (X = OAc, R = CH_3) with tri-*n*-butyltin fluoride followed by cycloaddition also only led to cyclopropanation. On the other hand,

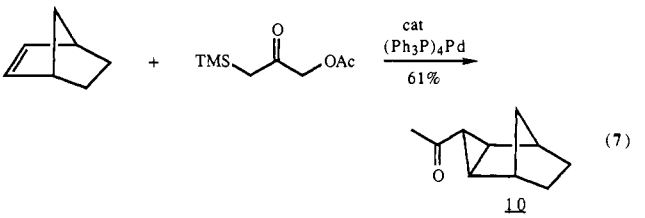


11a **11b** **12**

replacing the trimethylsilyl group by a methyl group as in **12** led to no cycloaddition.

The palladium catalyst required a phosphine or phosphite ligand. The $(dba)_3Pd_2{\cdot}CHCl_3$ complex in the absence of such a ligand fails to lead to cycloaddition. $Ni(cod)_2$ in the presence of triphenylphosphine fails to catalyze the reaction, although it is known to catalyze some cycloadditions involving trimethylenemethane.[14] On the other hand, solvents had a dramatic effect. Whereas the reaction time of 1 h was similar for benzene, THF, and acetonitrile, reaction was complete in 10 min in DMSO.

The reaction requires a strained double bond as present in norbornenes. Thus, norbornene itself is smoothly cyclopropanated (eq 7), although longer reactions times are required. The product



(7)

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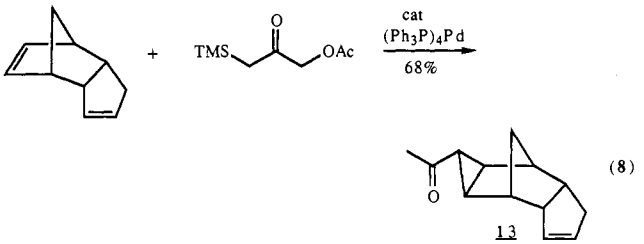
is identical with the compound obtained upon diimide reduction of the monoadduct of norbornadiene. Dicyclopentadiene undergoes cyclopropanation exclusively at the more strained double bond to form the single stereoisomeric adduct assigned as **13** by analogy to the above.



(8)

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Discussion

The present results support the working hypothesis that 1-acetoxy-3-(trimethylsilyl)propan-2-one may serve as a precursor to an (oxatrimethylenemethane)palladium complex according to eq 3 and 4. In accord with this hypothesis are the observations

(10) Friedman, O. M.; Seligman, A. M. *J. Am. Chem. Soc.* **1954**, *76*, 661. Fischer, E.; Fischer, H. O. L. *Chem. Ber.* **1914**, *47*, 771.

(11) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

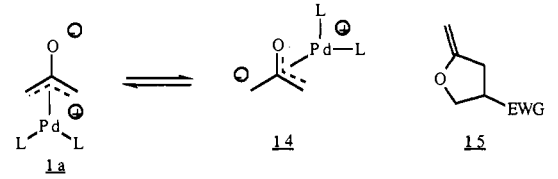
(12) Sauers, R. R.; Schlosberg, S. B.; Pfeffer, P. E. *J. Org. Chem.* **1968**, *33*, 2175.

(13) The *endo*-, *exo*- cyclopropylmethyl ketones that would arise from endo attack on norbornadiene and norbornene are known. See: Kirmse, W.; Olbricht, T. *Chem. Ber.* **1975**, *108*, 2629 and Creary, X. *J. Org. Chem.* **1975**, *40*, 3326, respectively.

(14) Jones, M. D.; Kemmett, R. D. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1201.

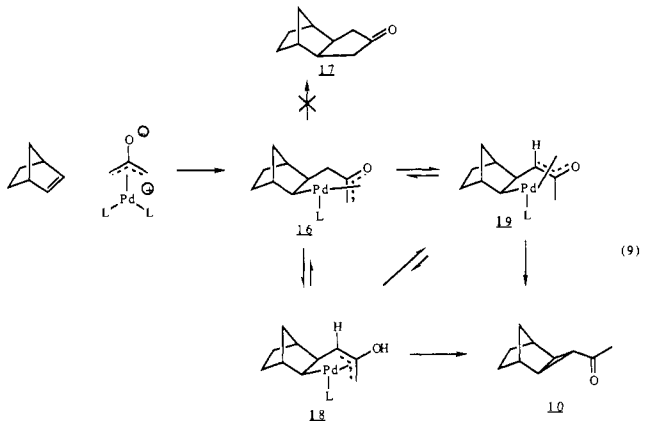
that (1) the oxygen must bear an easily cleavable group such as a silyl or stannyl group and (2) the leaving group must also be a good silylophile. These observations parallel the reactivity pattern for the (trimethylenemethane)palladium system.[1,2,15] Of particular note is the dependence of the cycloaddition on the nature of the leaving group. In neither case does chloride serve as a leaving group, presumably because of its poor silylophilic properties. The fact that Kemmitt et al. have been able to isolate the platinum complex **5** from **3** (X = Cl, R = CH_3) also supports the above interpretation.

The failure to effect cycloadditions to electron-deficient olefins, is, at first glance, surprising. In terms of the tautomeric zwitterionic structures **1a** and **14**, cyclopentanone annulation requires



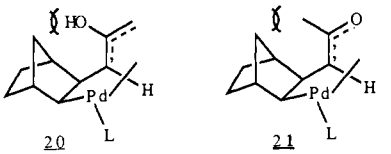
cycloaddition via **14**. The anticipated thermodynamic bias for **1a**[16] may be sufficiently large to make **14** inaccessible. The generally recognized poor ability of oxygen to serve as a Michael donor makes cycloadditions via **1a**, which should produce 2-methylenetetrahydrofurans such as **15**, less likely.[17]

In the absence of the ability of **1** to function as a 1,3-dipole in cycloadditions, an unexpected and strikingly different course is followed—cyclopropanation. The reactivity profile of **1** can be understood on the basis of its functioning as an unusually substituted π-allylpalladium cationic complex. In intermolecular reactions, π-allylpalladium complexes are known to be able to add only to strained double bonds in which norbornene is the outstanding example.[18-20] The first step in the cyclopropanation reaction may be the same as depicted in eq 9. Whereas, we depict



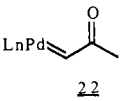
structures **16**, **18**, and **19** as oxa-π-allyl complexes for simplicity, the corresponding σ-complexes must be considered as likely alternatives. In such a scheme, we must assume that the reductive elimination of **16** to the cyclopentanone **17** must be slow compared to prototropic shift to complexes **18** and/or **19**.[21] Such a prototropic shift may involve the palladium or may arise by protonation followed by deprotonation. Reductive elimination from either **18** or **19** then generates the observed product.

This scheme nicely accommodates our experimental observations. For example, the beneficial effect of DMSO may be rationalized. The ability of DMSO to increase the electrophilic nature of π-allylpalladium complexes has been previously noted in allylic alkylations proceeding through such species.[22] This solvent should also facilitate prototropic shift either by palladium or by protonation–deprotonation. The exo,exo stereochemistry of the cyclopropanes is also accounted for by (1) the known preference for π-allyl complexes to react in an exo direction with respect to the norbornene[18-20] and (2) the greater stability of **18** and **19** compared to **20** and **21** due to the presence of severe



nonbonded interactions in these latter two complexes. The former point is particularly noteworthy in the case of norbornadiene since vinylpalladium complexes add in an endo selective manner with this diene in contrast to π-allylpalladium complexes.[23]

An alternative explanation considers an initial formation of a carbene palladium complex such as **22** either directly from **4** or



via rearrangement of the oxatrimethylenemethane complex **1**. In the palladium-catalyzed reactions of diazo compounds with olefins, such species appear likely.[24-27] Cyclopropanation occurs with many olefinic types. With diazomethane and palladium acetate, a preference for electron-deficient, strained, or conjugated olefins has also been noted.[25] The strikingly different reactivity profile makes such an intermediate unlikely in the present case.

While it appears that the original supposition that we could generate an (oxatrimethylenemethane)palladium complex from 1-acetoxy-3-(trimethylsilyl)-2-propanone is correct, such a palladium complex does not undergo cyclopentanone annulation in contrast to the all-carbon analogue. The remarkable cyclopropanation that occurs instead, while limited to strained double bonds such as the norbornenes examined herein, does have some synthetic utility as well as mechanistic and theoretical interest. For example, the high exo,exo stereoselectivity observed with norbornadiene stands in contrast to carbene additions to this diene[26,28] although the reaction of diazomethane in the presence

(15) For example, 2-(chloromethyl)-3-(trimethylsilyl)-1-propene fails to undergo Pd(0) catalyzed [3 + 2] cycloadditions to electron-deficient double bonds. On the other hand, if a stoichiometric amount of tetra-*n*-butylammonium acetate is added to the above, cycloaddition may even occur at room temperature. Trost, B. M.; Miller, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 3687.

(16) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. Trost, B. M.; Verhoeven, T. R. *Compr. Organomet. Chem.* **1982**, *8*, 799.

(17) For some exceptions, see: Ko, S. S.; Klein, L. L.; Pfaff, K.-P.; Kishi, Y. *Tetrahedron Lett.* **1982**, *23*, 4415. Dikshit, D. K.; Kapil, R. S.; Anand, N. *Ind. J. Chem.* **1975**, *13*, 1353, 1359. Harrison, I. T.; Fletcher, V. R.; Fried, J. H. *Tetrahedron Lett.* **1974**, 2733. Vlattas, I.; Lee, A. O. *Tetrahedron Lett.* **1974**, 4451. Vlattas, I.; Vecchia, L. D. *Tetrahedron Lett.* **1974**, 4451. Schweizer, E. E. *J. Am. Chem. Soc.* **1964**, *86*, 2744.

(18) Hughes, R. D.; Powell, J. *J. Organomet. Chem.* **1973**, *60*, 387, 427.

(19) Also see: Gallazzi, M. C.; Hanlon, T. L.; Vitulli, G.; Porri, L. *J. Organomet. Chem.* **1971**, *33*, C45. Zocchi, M.; Tieghi, G.; Albinati, A. *J. Organomet. Chem.* **1971**, *33*, C47; *J. Chem. Soc., Dalton Trans.* **1973**, 883. Dahan, F. *Acta Crystallogr. B* **1976**, 1941.

(20) Larock, R. D.; Burkhart, J. P.; Oertle, K. *Tetrahedron Lett.* **1982**, *23*, 1071.

(21) A reductive elimination involving an oxa-π-allylpalladium species is presumably involved in a palladium-catalyzed arylation of ketones. See: Kuwajima, I.; Urabe, H. *J. Am. Chem. Soc.* **1982**, *104*, 6831.

(22) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416, 3426.

(23) Larock, R. C.; Hershberger, S. S.; Takagi, K.; Mitchell, M. A. *J. Org. Chem.* **1986**, *51*, 2450. Vedejs, E.; Weeks, P. D. *Tetrahedron Lett.* **1974**, 3207.

(24) For a review, see: Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.

(25) (a) Mende, O.; Radüchel, B.; Skuballa, W.; Vorbrüggen, H. *Tetrahedron Lett.* **1975**, 629. (b) Radüchel, B.; Mende, U.; Cleve, G.; Hoyer, G. A.; Vorbrüggen, H. *Tetrahedron Lett.* **1975**, 633. (c) Kottwitz, J.; Vorbrüggen, H. *Synthesis* **1975**, 636. (d) For an exception, see: Suda, M. *Synthesis* **1981**, 714.

(26) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssié, P. *J. Org. Chem.* **1980**, *45*, 695.

(27) (a) Doyle, M. P.; Wang, L. C.; Loh, K. L. *Tetrahedron Lett.* **1984**, *25*, 4087. (b) Tomilov, Y. V.; Bordakov, V. G.; Dolgii, I. E.; Nefedov, O. M. *Izv. Akad. Nank SSSR, Ser. Khim.* **1984**, 582; Chem. Abstr. **1984**, *101*, 90447*g*.

of palladium acetate is reported to produce bis-*exo*-cyclopropane.[25c,27b]

Experimental Section

1-Acetoxy-3-(trimethylsilyl)-2-propanone (4) (X = OAc, R = CH_3). [(Trimethylsilyl)methyl]magnesium chloride [prepared from 6.1 g (50 mmol) of (trimethylsilyl)methyl chloride, 1.22 g (50 mmol) of magnesium turnings and one crystal of iodine in 60 mL of ether] was added dropwise to 10.9 g (50 mmol) of acetoxyacetic anhydride in 60 mL of ether at −78 °C. The mixture was kept at −78 °C for 2 h, warmed to 0 °C within 10 min, and hydrolyzed immediately with 100 mL of aqueous saturated sodium bicarbonate solution. The two-phase system was stirred until the evolution of carbon dioxide ceased. The aqueous layer was extracted with 100 mL of ether once. The combined organic layers were dried with sodium sulfate. After evaporation of the solvent, the residue was fractionally distilled under reduced pressure to give 5.3 g (56%) of the title compound, bp 75 °C (1 Torr). IR ($CHCl_3$): 1745, 1710, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): δ 4.57 (s, 2 H), 2.20 (s, 2 H), 2.17 (s, 3 H), 0.16 (s, 9 H). Calcd for $C_8H_{16}O_3Si$: 188.0869. Found: 188.0867.

1-[(Methoxycarbonyl)oxy]-3-(trimethylsilyl)-2-propanone (4) (X = OCO_2CH_3, R = CH_3). An identical procedure to the above but utilizing 50 mmol of the mixed anhydride derived from [(methoxycarbonyl)-oxy]acetic acid and methyl chloroformate gave 1.59 g (16%) of the title compound, bp 89 °C (1 Torr). IR ($CHCl_3$): 1740, 840 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): δ 4.58 (s, 2 H), 3.83 (s, 3 H), 2.22 (s, 2 H), 0.17 (s, 9 H).

1-Acetoxy-3-(dimethylphenylsilyl)-2-propanone (4) (X = OAc, R = Ph). An identical procedure to the above but utilizing [(dimethylphenylsilyl)methyl]magnesium chloride gave 11.1 g (89%) of the title compound, bp 135 °C (0.5 Torr). IR ($CDCl_3$): 1745, 1710, 1370, 1195 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): δ 7.56-7.49 (m, 2 H), 7.43-7.35 (m, 3 H), 4.38 (s, 2 H), 2.40 (s, 2 H), 2.10 (s, 3 H), 0.44 (s, 6 H). Calcd for $C_7H_{13}O_3Si$: 173.0634. Found: 173.0635.

General Cyclopropanation. All reactions were run on a 1.0-mmol scale. To a mixture of 188 mg (1.0 mmol) of the silyl acetate **4** (X = OAc, R = CH_3) and 2.0 mmol of the olefin was added 0.5 mL (5 mol %) of a freshly prepared catalyst solution [catalyst solution: 260 mg (0.25 mmol) of $dba_3Pd_2{\cdot}CHCl_3$ and 524 mg (2.0 mmol) of triphenylphosphine in 5 mL of benzene-d_6]. The mixture was heated to 80 °C whereby enol silyl ether forms in less than 1 min. After complete disappearance of enol silyl acetate as determined by NMR spectroscopy, 1 h for norbornadiene, 20 h for norbornene, and 2 h for dicyclopentadiene, the mixture was filtered through a pad of silica gel and washed with ether. Flash chromatography on silica gel with 1:2 (v/v) ether/hexane as eluant gave the pure products.

Cyclopropanation of Norbornadiene. 3-Acetyltricyclo[3.2.1.$0^{2,4}$]-6-octene (8). Yield: 83 mg (56%) of oil that crystallizes at −12 °C. IR ($CDCl_3$): 1685 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): δ 6.41 (m, 2 H), 2.92 (m, 2 H), 2.86 (t, J = 2.2 Hz, 1 H), 2.19 (s, 3 H), 1.67 (m, 2 H), 1.18 (dm, J = 9.9 Hz, 1 H), 1.03 (dm, J = 9.9 Hz, 1 H). Calcd for $C_{10}H_{12}O$: 148.0888. Found: 148.0882.

3,7-Diacetyltetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane (9). Yield: 16.9 mg (17%) of crystalline solid, mp 154-5 °C. IR ($CDCl_3$): 1690 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 2.55 (m, 2 H), 2.31 (m, 2 H) 2.17 (s, 6 H), 1.69 (m, 4 H), 0.57 (m, 2 H). Calcd for $C_{13}H_{16}O_2$: 204.1150. Found: 204.1158.

Cyclopropanation of Norbornene. 3-Acetyltricyclo[3.2.1.$0^{2,4}$]octane (10). Yield: 91 mg (61%) of crystalline solid, mp 39-41 °C (lit. mp 38-40 °C). IR ($CDCl_3$): 1690 cm^{-1}. ^1H NMR: δ 2.27 (m, 2 H), 2.11 (s, 3 H), 1.80 (m, 1 H), 1.29 (m, 2 H), 1.40-1.20 (m, 4 H), 0.86 (dm, J = 10.9 Hz, 1 H), 0.62 (dm, J = 10.9 Hz, 1 H). Calcd for $C_{10}H_{14}O$: 150.1045. Found: 150.1049.

Cyclopropanation of Dicyclopentadiene. 9-Acetyltetracyclo[5.3.1.$0^{2,6}$.$0^{8,10}$]-3-undecane (13). Yield: 128 mg (68%) of oil. IR ($CDCl_3$): 1685 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): δ 5.73 (dm, J = 5.8 Hz, 1 H), 5.54 (dm, J = 5.8 Hz, 1 H), 2.16 (s, 3 H), 2.35-2.15 (m, 3 H), 3.10 (m, 1 H), 2.57 (m, 1 H), 2.42 (1 H, m), 1.96 (1 H, m), 1.52 (dm, J = 7.0 Hz, 1 H), 1.23 (dm, J = 7.0 Hz, 1 H), 1.08 (dm, J = 10.6 Hz, 1 H), 0.94 (dm, J = 10.6 Hz, 1 H). Calcd for $C_{13}H_{16}O$: 188.1183. Found: 188.1188.

Diimide Reduction of 8. Hydrazine hydrate (1.2 mL) was added to a solution of 15 mg (0.1 mmol) of olefin **8** in 1.2 mL of ethanol containing 5 mg of cupric acetate. After stirring for 24 h at room temperature, at which point TLC indicated complete conversion, the mixture was extracted with hexane. The hexane extracts were washed with water, dried over sodium sulfate, evaporated in vacuo, and chromatographed through a short column of silica gel with 1:2 (v/v) of ether/hexane as eluant to give pure saturated ketone **10**.

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(28) Sauers, R. R.; Sonnet, P. E. *Tetrahedron* **1964**, *20*, 1029.

Effect of Through-Bond Interaction on Conformation and Structure of Some *N*-Arylpiperidone and *N*-Aryltropanone Derivatives. 2[1]

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Abstract: Through-bond interaction (TBI) in *N*-aryl-4-piperidone derivatives in which the carbonyl group is modified to enhance its electron deficiency is found to stabilize the sterically disfavored axial arrangement of the aryl group, an arrangement also found in the corresponding tropanone derivatives, where it may, however, be favored sterically. In the *N*-arylpiperidone derivatives the relative stability of conformations with axial and equatorial orientation of the phenyl group is markedly influenced by para substitution in the aryl group thus indicating the possibility of long-range stereoelectronic conformational control mediated by through-bond interaction across three σ-bonds. Theoretical predictions regarding the influence of TBI on bond lengths are confirmed in the crystal structures of the compounds studied, while strong TBI is also found to result in significant pyramidalization at C4.

The term through-bond interaction (TBI) was introduced in 1968 by Hoffmann et al.[2,3] to designate the intramolecular interaction between functional groups via the intervening σ-bonds. Theoretical studies[2-5] show that, e.g., the TBI between two nitrogen lone pairs separated by three σ-bonds will be optimized for the

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(1) Krijnen, B.; Beverloo, H. B.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 135.

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