

mation concerning this out-of-plane trans effect are under way with analogous compounds.

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Registry No. [FeOHP]<sub>n</sub>, 87901-24-4.

**Supplementary Material Available:** Table of observed and calculated structure factors for [FeOHP]<sub>n</sub> (15 pages). Ordering information is given on any current masthead page.

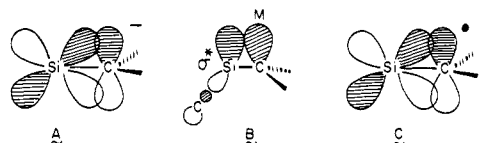
## Configurational Stability of the 2,2-Diphenyl-1-(trimethylsilyl)cyclopropyl Carbanion and Free Radical. Absolute Stereochemical Assignments to Select Silylcyclopropanes<sup>1</sup>

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Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. Received June 27, 1983

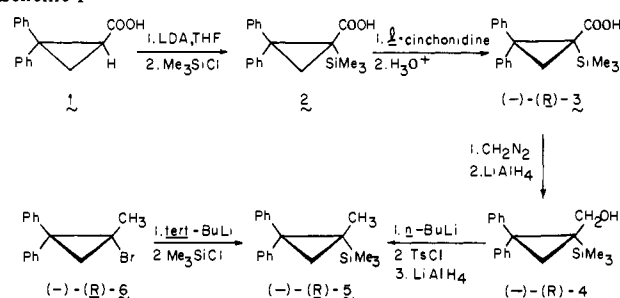
**Abstract:** 2,2-Diphenylcyclopropanecarboxylic acid was silylated at the 1-position and this product was resolved with *l*-cinchonidine. The resulting optically active acid was transformed into (–)-2,2-diphenyl-1-methyl-1-(trimethylsilyl)cyclopropane, whose absolute configuration was shown to be *R* by metalation and silylation of (–)-(*R*)-**6**. The latter reaction proceeds with retention of configuration. In this way, the levorotatory form of (–)-**3** was established to be *R*. Whereas the Hunsdiecker degradation of (–)-(*R*)-**3** produced only racemic bromide, application of the Haller–Bauer process to (+)-(*R*)-phenyl ketone **12** led to (–)-(*R*)-silane **13**. That this carbanion-mediated reaction proceeded with complete retention of stereochemistry was confirmed by preparation of (+)-1-(*S*)-3-(*S*)-**16** and X-ray analysis of its *l*-menthyl ester (**17**), in tandem with suitable transformation of (–)-1-(*R*)-3-(*R*)-**16** to the identical levorotatory silane **13**. The failure of the α-silyl cyclopropyl free radical to maintain configuration and the nonracemizability of its carbanion counterpart are discussed in the light of silicon's capacity for stabilizing neighboring reactive centers.

Although α-silyl carbanions are gaining increased importance in synthesis,<sup>3</sup> the manner in which silicon stabilizes adjacent carbon–metal bonds remains unclear. The electron-attracting capability of R<sub>3</sub>Si substituents, which overrides the greater electropositive character of silicon relative to carbon, has been recognized for many years.<sup>4</sup> Early rationalizations of this stabilizing influence favored a d<sub>x</sub>–p<sub>x</sub> model (A) wherein overlap of



an empty d orbital on Si having the proper symmetry with the filled carbanion orbital leads to a decrease in energy. Although such thinking remains popular,<sup>5</sup> an alternative explanation has been advanced which discounts the importance of d orbitals. According to the latter argument, an empty σ\* orbital on Si can

Scheme I



overlap adequately well with the filled orbital of a covalent carbon–metal bond (B) to account for the stabilization.<sup>6,7</sup> The importance of n<sub>C</sub>–σ\*<sub>SR</sub> charge-transfer interactions to α-thia carbanions has been studied in depth by perturbation MO methods,<sup>8</sup> and it may well be that polarization of the C–Si bond in the C<sup>δ</sup>–Si<sup>δ+</sup> direction is adequate to guarantee the level of stabilization encountered.

(1) Silanes in Organic Synthesis. 21. For part 20, see: Paquette, L. A.; Charumilind, P.; Gallucci, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 7364.

(2) (a) Postdoctoral Researcher on sabbatical leave from Fukui University, Bunkyo, Fukui 910, Japan. (b) Author to whom inquiries concerning the X-ray crystal structure analysis should be directed.

(3) Magnus, P. *Aldrichimica Acta* **1980**, *13*, 43.

(4) For some early examples, consult: (a) Eaborn, C. "Organosilicon Compounds"; Butterworths: London, 1960. (b) Bazant, V.; Chvalovsky, V.; Rathousky, J. "Organosilicon Compounds"; Academic Press: New York, 1965; Vol. 1. (c) Bott, R. W.; Eaborn, C. In "Organometallic Compounds of the Group IV Elements"; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1, Part 1, Chapter 2.

(5) Kwart, H.; King, H. G. "d-Orbitals in the Chemistry of Silicon, Phosphorus, and Sulfur"; Springer-Verlag: New York, 1977.

(6) (a) Pitt, C. G. *J. Organometal. Chem.* **1973**, *61*, 49. (b) Enslin, W.; Bock, H.; Becker, G. *J. Am. Chem. Soc.* **1974**, *96*, 2757. (c) Jung, I. N.; Jones, P. R. *J. Organometal. Chem.* **1975**, *101*, 27, 35. (d) Ponoc, R.; Chernyshev, E. A.; Tolstikova, N. G.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2714. (e) Reynolds, W. F.; Hamer, G. K.; Bassindale, A. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 971. (f) Ramsey, B. G. *J. Organometal. Chem.* **1977**, *135*, 307. (g) Adcock, W.; Aldous, G. L.; Kitching, W. *Tetrahedron Lett.* **1978**, 3387.

(7) (a) Fleming, I. In "Comprehensive Organic Chemistry"; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, Chapter 13. (b) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981.

(8) (a) Epiotis, N. D.; Yates, R. L.; Bernardi, F.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 5435. (b) Lehn, J.-M.; Wipff, G. *Ibid.* **1976**, *98*, 7498.

$\alpha$ -Silyl radicals have been less well studied.<sup>9,10</sup> Multiple bonding between the ligand and silicon via  $p_x$ - $d_x$  conjugation (see C) is thought to prevail here.

The present paper describes an experimental study designed to probe both of these questions. Where  $\alpha$ -silyl carbanions are concerned, stabilization as in A can arise only when a relatively free carbanion is involved and  $sp^2$  character is fully developed on carbon. On the other hand,  $n_C$ - $\sigma^*_{SiR_3}$  charge transfer as exemplified by B is best served if the metal-carbon bond remains intact and tetrahedral status is retained. Comparable hybridization arguments apply to the related free radicals. Since several cyclopropyl carbanions derived from optically active precursors are capable of retaining their optical activity and configuration to a large degree,<sup>11,12</sup> it is clear that I strain effects deter planarization at carbon in these systems. The corresponding free radicals have been found to be somewhat less constrained, the levels of racemization being inherently more dependent on the electronegativity of the 1-substituent.<sup>13</sup>

Accordingly, a number of optically active silyl-substituted cyclopropanes have been prepared and their absolute configurations determined. The fate of the derived carbanion and free radical has been examined with the intent of gaining insight into the balance of forces which become operative as the direct result of silicon substitution.

## Results

**2,2-Diphenyl-1-(trimethylsilyl)cyclopropanecarboxylic Acid. Stereochemical Correlations.** The synthesis of **1** has previously been described.<sup>12a</sup> To arrive at **2** (Scheme I), use was made of earlier findings<sup>14</sup> that dianions of cyclopropanecarboxylic acids bypass customary oxyanion nucleophilicity and undergo regio-specific C-silylation upon reaction with chlorotrimethylsilane. The development of methylene cyclopropane character is thereby avoided. Because the steric contributions of the two flanking phenyl groups lower the efficiency of this process (21% of **2**), an alternative 1,3-dipolar approach<sup>15</sup> was briefly investigated.

(9) (a) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 6161. (b) Kawamura, T.; Kochi, J. K. *Ibid.* **1972**, *94*, 648.

(10) Mackey, J. H.; Wood, D. E. *Mol. Phys.* **1970**, *18*, 783.

(11) (a) *1-Methyl*: Walborsky, H. M.; Impastato, F. J. *J. Am. Chem. Soc.* **1959**, *81*, 5835. Walborsky, H. M.; Young, A. E. *Ibid.* **1961**, *83*, 2595; *Ibid.* **1964**, *86*, 3288. Impastato, F. J.; Walborsky, H. M. *Ibid.* **1962**, *84*, 4328. Walborsky, H. M.; Impastato, F. J.; Young, A. E. *Ibid.* **1964**, *86*, 3283. Pierce, J. B.; Walborsky, H. M. *J. Org. Chem.* **1968**, *33*, 1962. Walborsky, H. M.; Johnson, F. P.; Pierce, J. B. *J. Am. Chem. Soc.* **1968**, *90*, 5222. Webb, J. L.; Mann, C. K.; Walborsky, H. M. *Ibid.* **1970**, *92*, 2042. (b) *1-Isocyanato*: Walborsky, H. M.; Periasamy, M. P. *Ibid.* **1974**, *96*, 3711. Periasamy, M. P.; Walborsky, H. M. *Ibid.* **1975**, *97*, 5930; *Ibid.* **1977**, *99*, 2631. (c) *1-Chloro-1-fluoro, and 1-methoxy*: Walborsky, H. M.; Allen, L. E.; Traenckner, H.-J.; Powers, E. J. *J. Org. Chem.* **1971**, *36*, 2937. (d) *1-Phenyl*: Hoell, D.; Schnieders, C.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 243.

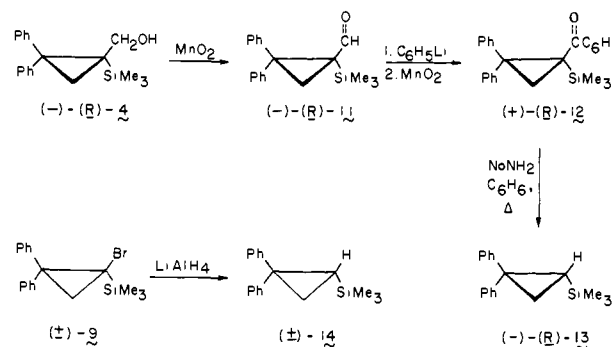
(12) The situation can be quite different when groups capable of resonance delocalization are involved: (a) *1-Cyano*: Walborsky, H. M.; Hornyak, F. M. *J. Am. Chem. Soc.* **1955**, *77*, 6026; **1956**, *78*, 872. Walborsky, H. M.; Yousef, A. A.; Motes, J. M. *Ibid.* **1962**, *84*, 2465. Walborsky, H. M.; Motes, J. M. *Ibid.* **1970**, *92*, 2445. (b) *1-Benzoyl*: Motes, J. M.; Walborsky, H. M. *Ibid.* **1970**, *92*, 3697.

(13) (a) Walborsky, H. M.; Chen, C.-J.; Webb, J. L. *Tetrahedron Lett.* **1964**, 3551. (b) Walborsky, H. M.; Chen, C.-J.; *J. Am. Chem. Soc.* **1967**, *89*, 5499. (c) Walborsky, H. M.; Collins, P. C. *J. Org. Chem.* **1976**, *41*, 940. (d) Walborsky, H. M.; Allen, L. E. *J. Am. Chem. Soc.* **1971**, *93*, 5465. (e) Ando, T.; Ishihara, T.; Yamashita, A.; Matsumoto, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3873. (f) Ando, T.; Yamashita, A.; Matsumoto, M.; Ishihara, T.; Yamanaka, H. *Chem. Lett.* **1973**, 1133. (g) Ishihara, T.; Hayashi, K.; Ando, T.; Yamanaka, H. *J. Org. Chem.* **1975**, *40*, 3264. (h) Applequist, D. E.; Peterson, A. H. *J. Am. Chem. Soc.* **1960**, *82*, 2372. (i) Ando, T.; Yamanaka, H.; Namigata, F.; Funasaka, W. *J. Org. Chem.* **1970**, *35*, 33. (k) Altman, L. J.; Vederas, J. C. *Chem. Commun.* **1969**, 895. (l) Altman, L. J.; Baldwin, R. C. *Tetrahedron Lett.* **1971**, 2531. (m) Hatem, J.; Waegell, B. *Ibid.* **1973**, 2019. (n) Groves, J. T.; Ma, K. W. *J. Am. Chem. Soc.* **1974**, *96*, 6527. (o) Singer, L. A.; Chen, J. *Tetrahedron Lett.* **1971**, 939. (p) Kobayashi, K.; Lambert, J. B. *J. Org. Chem.* **1977**, *42*, 1254. (q) Boche, G.; Schneider, D. R.; Wintermayr, H. *J. Am. Chem. Soc.* **1980**, *102*, 5697.

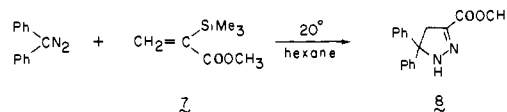
(14) (a) Ainsworth, C.; Kuo, Y.-N. *J. Organometal. Chem.* **1972**, *46*, 73. (b) Warner, P. M.; Le, D. *J. Org. Chem.* **1982**, *47*, 893.

(15) This procedure has been utilized effectively with  $\alpha$ -methyl,  $\alpha$ -bromo,  $\alpha$ -chloro,  $\alpha$ -methoxy, and  $\alpha$ -fluoro acrylate esters.<sup>11,13</sup> The addition of diphenyldiazomethane to (trimethylsilyl)vinylsilane has also been reported [D'yakonov, I. A.; Golodnikov, G. V.; Repinskaya, I. B. *Zh. Org. Khim.* **1965**, *1*, 220].

## Scheme II



However, reaction of diphenyldiazomethane with **7**<sup>16</sup> produced the known pyrazoline **8**<sup>17</sup> via in situ desilylation and was not serviceable.



*l*-Cinchonidine allowed for the ready resolution of **2**; the levorotatory enantiomer was present in the less soluble diastereomeric salt. The absolute configuration of  $(-)$ -**3** was established as *R* by conventional chemical transformation to the methyl derivative  $(-)$ - $(R)$ -**5**, which was synthesized independently from the known  $(-)$ - $(R)$ -**6**.<sup>18</sup> A sample of this bromide having  $[\alpha]_D^{22.5}$   $-108.2^\circ$  in chloroform and an optical purity of 98%<sup>18</sup> was subjected to halogen-metal exchange with *tert*-butyllithium under conditions known to preserve configuration. The ensuing silylation gave samples of **5** which exhibited  $[\alpha]_D^{22.5}$  values of  $-58.6^\circ$  in chloroform. If the assumption is made that the conversion of **6** to **5** proceeds without configurational loss as anticipated, it can be estimated on the basis of the  $[\alpha]_D$  of **5** obtained from  $(-)$ -**3** ( $-57.6^\circ$ ) that our resolved acid has an optical purity of 96%.

**Hunsdiecker Degradation.** The Hunsdiecker reaction was the method chosen for generation of the 2,2-diphenyl-1-(trimethylsilyl)cyclopropyl free radical. Two procedures are most frequently used to achieve this halogenative decarboxylation.<sup>19</sup> In the first, the carboxylic acid is treated directly with red mercuric oxide and bromine in carbon tetrachloride as solvent.<sup>20</sup> Upon exposure to this reagent combination at the reflux temperature,  $(-)$ - $(R)$ -**3** was transformed in 59% yield into essentially racemic bromide **9**. Decarboxylation was also rapid at 0 °C, but complete loss of configuration stability was again seen. Consequently, recourse was made to the preparation of dry, optically active silver salt **10** and its subsequent reaction at 0 °C with bromine in the same solvent system.<sup>21</sup> These conditions also led to the isolation of racemic bromide.

**Attempted Decarbonylation of the Aldehyde.** When aldehydes are treated with tris(triphenylphosphine)rhodium chloride, oxidative addition occurs with formation of an acyl rhodium com-

(16) Billingham, N. C.; Jenkins, A. D.; Kronfli, E. B.; Walton, D. R. M. *J. Polym. Sci. Polym. Chem. Ed.* **1977**, *15*, 683.

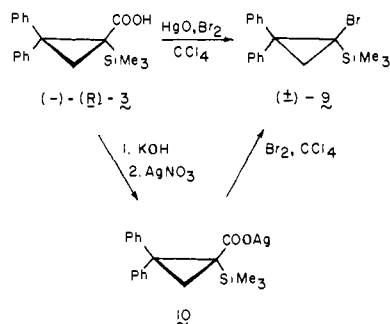
(17) (a) Jones, W. M.; Sanderfer, P. O.; Baarda, D. G. *J. Org. Chem.* **1969**, *32*, 1367. (b) Brey, W. S.; Valencia, C. M. *Can. J. Chem.* **1968**, *46*, 810.

(18) (a) Reference 11a, fourth citation. (b) Walborsky, H. M.; Banks, R. B.; Banks, M. L. A.; Duraisamy, M. *Organometallics* **1982**, *1*, 667.

(19) At least two other modifications exist. The first involves the action of bromine upon a thallium(I) salt [McKillop, A.; Bromley, D.; Taylor, E. C. *J. Org. Chem.* **1969**, *34*, 1172. Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 7218]. The second entails reaction of a carboxylic acid with lead tetraacetate and a halide species [Sheldon, R. A.; Kochi, J. K. *Org. React.* **1972**, *19*, 279].

(20) (a) Cristol, S. J.; Firth, W. C. *J. Org. Chem.* **1961**, *26*, 280. (b) Cristol, S. J.; Douglass, J. R.; Firth, W. C.; Krell, R. E. *Ibid.* **1962**, *27*, 2711. (c) Meek, J. S.; Osuga, D. T. *Org. Synth.* **1963**, *43*, 9. (d) Lampman, G. M.; Aumiller, J. C. *Ibid.* **1971**, *51*, 106. (e) Paquette, L. A.; Wells, G. J.; Horn, K. A.; Yan, T.-H. *Tetrahedron* **1983**, *39*, 913.

(21) Wilson, C. V. *Org. React.* **1957**, *9*, 332.



plex.<sup>22</sup> This intermediate subsequently collapses to hydrocarbon product via an intramolecular free-radical pathway involving cleavage and disproportionation.<sup>19d,23</sup> Walborsky and Allen have determined that the decarbonylation of several 1-substituted cyclopropyl aldehydes in this manner delivers products having optical purities varying from 86% to 6%.<sup>13d</sup> With the intent of generating the 2,2-diphenyl-1-(trimethylsilyl)cyclopropyl radical in an alternative manner, (-)-(R)-aldehyde **11** was prepared by manganese dioxide oxidation<sup>24</sup> of (-)-(R)-**4**. Unfortunately, however, **11** proved to be inert to Wilkinson's catalyst in a variety of solvents (toluene, xylene, benzonitrile, *N,N*-dimethylacetamide, etc.) up to their reflux temperatures. Evidently, the steric bulk of the trimethylsilyl substituent is adequate to deter the prerequisite oxidative addition step.

**Haller-Bauer Cleavage of the Phenyl Ketone.** The Haller-Bauer reaction<sup>25</sup> has played a prominent role in the study of cyclopropyl anions and was consequently adapted to the present context. In the case of the 1-methyl derivative, deacylation proceeds stereospecifically to give optically pure hydrocarbon with retention of configuration.<sup>26</sup> Optical activity is also retained with 1-chloro, 1-fluoro, and 1-methoxy substitution, although the precise stereochemical course of events was not unequivocally established.<sup>11c</sup> For reasons outlined in the introduction, it was not clear what the effect of silyl substitution would have on the configurational outcome of the reaction.

To investigate this question, (-)-(R)-**11** was sequentially condensed with phenyllithium and oxidized with manganese dioxide to give (+)-(R)-**12** (Scheme II). Cleavage of this optically active phenyl ketone with sodium amide in refluxing benzene gave rise to optically active **13**,  $[\alpha]^{22.5}_D -167^\circ$  in chloroform. The spectral properties of this silane proved identical with those of racemic **14** prepared by lithium aluminum hydride reduction of racemic bromide **9**.

It remained to determine the extent to which optical activity had been retained in product **13** and whether inversion or retention of configuration had occurred.

**Absolute Configuration of 2,2-Diphenyl-1-(trimethylsilyl)-cyclopropane.** The first of these pivotal issues was answered by making recourse to an alternative preparation of (-)-(R)-**13** (Scheme III). The known racemic carboxylic acid **15**<sup>27</sup> was also well resolved with *l*-cinchonidine. A sample of dextrorotatory enantiomer (+)-**16**,  $[\alpha]^{22.5}_D +285^\circ$ , was transformed via its acid chloride to the nicely crystalline *l*-menthyl ester (+)-**17** which was subjected to X-ray analysis. The absolute configuration of the molecule was fixed by the known configuration of the *l*-menthol group. On the basis of the X-ray structure, the configuration of (+)-**16** must be 1-(S)-3-(S). The cyclohexane ring of the *l*-menthol group is in the chair conformation with all substituents equatorial. The carbonyl group is not quite eclipsed by the axial hydrogen, H(6), with a torsion angle of  $24^\circ$  for O(2)-C(11)-C(6)-H(6). This conformational feature has been observed and commented on in previous structural studies of ester groups in

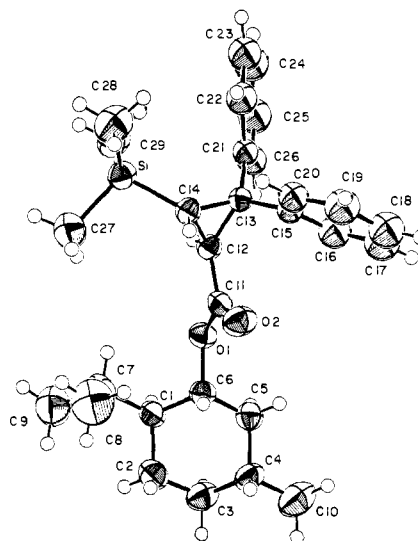
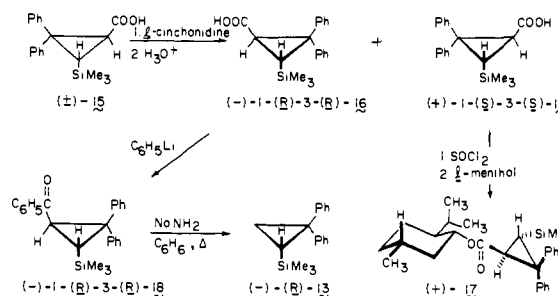


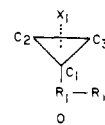
Figure 1. ORTEP drawing for (+)-**17**. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Hydrogen atoms are drawn artificially small.

### Scheme III



equatorial positions of cyclohexane rings.<sup>28,29</sup> The carbonyl group is trans to the cyclopropyl ring hydrogen, H(12), with a torsion angle of  $-177^\circ$  for H(12)-C(12)-C(11)-O(2). Furthermore, the connection between the two rings is essentially planar with a torsion angle of  $-171^\circ$  for C(12)-C(11)-O(1)-C(6) (Figure 1).

The cyclopropane ring can best be described as an isosceles triangle with the trimethylsilyl and carboxylate groups disposed on opposite sides of the ring. Although the bond lengths are not significantly different, the observed asymmetry may reflect the influences of the acceptor and donor substituents. The mean C-C distance in this ring is 1.503 (18) Å. The conformation of substituents on a cyclopropane ring can be described in terms of the torsion angle,  $\tau$ , defined as X(1)-O(X)-R(1)-R(11), where X(1) is the midpoint of the distal C(2)-C(3) bond (as in D).<sup>30</sup> The



carbonyl group with a  $\tau$  value of  $29.9^\circ$  for X-C(12)-C(11)-O(2) is in the *cis gauche* conformation. This angle is within the range of  $\tau$  limits for effective electron density transfer from cyclopropane to a carbonyl group.<sup>29</sup>

The sterically imposed conformation of the phenyl rings is similar to that observed for other *gem*-diphenyl cyclopropanes.<sup>31</sup> The dihedral angle between the phenyl rings is  $108^\circ$ . Both rings are close to the perpendicular conformation defined as  $\tau = 90^\circ$ ,

(22) Tsuji, J.; Ohno, K. *Tetrahedron Lett.* **1965**, 3962. Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, 90, 99.

(23) Tsuji, J.; Ohno, K. *Synthesis* **1969**, 157.

(24) Ohkata, K.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, 102, 1082.

(25) Hamlin, K. E.; Weston, A. W. *Org. React.* **1957**, 9, 1.

(26) Reference 11a, third citation.

(27) Cunico, R. F.; Lee, H. M. *J. Am. Chem. Soc.* **1977**, 99, 7613.

(28) Parthasarathy, R.; Ohrt, J.; Horeau, A.; Vigneron, J. P.; Kagan, H. B. *Tetrahedron* **1970**, 26, 4705.

(29) Mathieson, A. Mc. L. *Tetrahedron Lett.* **1965**, 4137.

(30) Allen, F. H. *Acta Crystallogr., Sect. B* **1980**, B36, 81.

(31) Lauher, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, 97, 561.

with respect to the cyclopropyl ring; the mean  $\tau$  values are 105.8° [C(20)-C(15)-C(13)-X = -74.1° and C(16)-C(15)-C(13)-X = 105.7°] and 105.0° [C(22)-C(21)-C(13)-X = 103.9° and C(26)-C(21)-C(13)-X = -73.9°].

In order to achieve direct correlation, a sample of (-)-1-(*R*)-3-(*R*)-**16**,  $[\alpha]^{22.5}_D -165^\circ$ , was transformed by reaction with phenyllithium into levorotatory phenyl ketone **18**. If the carboxylic acid utilized in the menthyl ester preparation is of 100% optical purity,<sup>32</sup> then the optical purity level of (-)-**18** is 58%. In this particular instance, Haller-Bauer degradation should not affect the trimethylsilyl-substituted chiral center. Since the product of this reaction, which exhibited an  $[\alpha]^{22.5}_D$  of -96° in chloroform, must possess the *R* configuration, the cleavage of (+)-**12** necessarily must have proceeded with retention of configuration. Furthermore, comparison of the specific rotations of the two silylcyclopropane samples suggests that a stereospecific pathway has indeed been followed.

## Discussion

The generation of a cyclopropyl radical at a silylated chiral center under Hunsdiecker conditions has been shown to result in complete loss of configuration prior to bromine atom capture. Although the unsubstituted cyclopropyl system prefers to exist as a bent  $\sigma$  radical,<sup>33-35</sup> configurational inversion through a  $\pi$  radical transition state is known to occur rapidly ( $\sim 10^8$  s<sup>-1</sup>) under certain circumstances. A neighboring Me<sub>3</sub>Si substituent is, therefore, unable to stabilize a pyramidal configuration. In this property,  $\alpha$ -silyl compares to  $\alpha$ -chloro and  $\alpha$ -methoxy but differs intrinsically from  $\alpha$ -fluoro. This loss of stereochemistry may arise from at least two divergent effects. In the first, the electropositive nature of silicon can be expected to decrease the *s* character of the orbital which contains the unpaired electron and thereby facilitate racemization.<sup>36,37</sup> Secondly, it is possible that  $\alpha$ -silyl radicals gain their inherent stability primarily from  $d_{\pi}$ - $p_{\pi}$  overlap as in C. A significant contribution of this type would again have the net effect of facilitating loss of configuration by favoring planar  $\pi$  radical status. While the delocalization in question differs from that operative with pendant carbonyl, cyano, and vinyl groups, the observable end result is the same. In the present context, it is not possible to dissect the relative importance of these two contributions; quite possibly, both effects are operative. The relatively large steric bulk of the Me<sub>3</sub>Si group should also favor loss of configuration.

Against this backdrop, the structurally related chiral  $\alpha$ -silyl cyclopropyl carbanion was found to be configurationally stable under Haller-Bauer conditions and to deliver product stereospecifically with complete retention. Since carbanions are well-known to intervene in these reactions,<sup>11c,25,26,38</sup> the maintenance of full optical purity during the conversion of phenyl ketone (+)-(*R*)-**12** to silane (-)-(*R*)-**13** requires that a reasonable barrier to planarization exist in the reactive intermediate. The results of these experiments clearly show that the  $\alpha$ -silyl cyclopropyl carbanion does not necessarily depend on  $d_{\pi}$ - $p_{\pi}$  overlap as in A for its stabilization. Stereoretention has previously been encountered with 1-chloro, 1-fluoro, 1-isocyano, 1-methoxy-, and 1-methyl cyclopropyl anions.<sup>11b,11c,26</sup> Thus, 1-trimethylsilyl substitution does not alter a predated behavioral pattern. The inevitable conclusion is that conjugative interaction of the type

modeled by A is not sufficiently important to override the preferred pyramidal character of the cyclopropyl anion. This finding does not, of course, confirm that  $n_C-\sigma^*_{SiR}$  charge transfer as in B operates; additional studies are required to substantiate this point. In particular, demonstration that the trimethylsilyl group is equally effective in stabilizing a carbanion in a less strained system would provide strong evidence for universal stabilization by structure B. Studies of this type are in progress.

The lack of kinetic acidity associated with  $\alpha$ -protons in silylcyclopropanes<sup>20e</sup> and our current inability to obtain bromide **9** in optically active form preclude more detailed examination of the configurational stability of  $\alpha$ -silyl cyclopropyl organometallic reagents at this time. Nevertheless, the high retention associated with the (+)-(*R*)-**12** to (-)-(*R*)-**13** conversion demands that Me<sub>3</sub>Si not lower the racemization barrier in this carbanionic system. Neither the electronegativity of the silyl substituent, the availability of empty *d* orbitals, nor the possibility of negative charge stabilization via resonance is a sufficient factor to foster cyclopropyl carbanion planarization and loss of optical activity through symmetrization.

## Experimental Section

Infrared spectra were obtained with a Perkin-Elmer Model 467 instrument. Proton magnetic resonance spectra were recorded with Varian T-60 and EM-390 spectrometers; apparent splittings are given in all cases. Mass spectra were determined on a Kratos MS-30 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Optical rotation data were determined on a Perkin-Elmer Model 241 polarimeter.

**2,2-Diphenyl-1-(trimethylsilyl)cyclopropanecarboxylic Acid (2).** A cold (0 °C), magnetically stirred solution of diisopropylamine (6.1 g, 60 mmol) in anhydrous tetrahydrofuran (30 mL) was treated dropwise under nitrogen with *n*-butyllithium (55 mL of 1.1 M in hexane, 60 mmol). After 25 min, a solution of **12a** (4.8 g, 20 mmol) in the same solvent (50 mL) was introduced dropwise during 50 min and the dianion solution was stirred at 0 °C for 3 h. The cold reaction mixture was treated dropwise with chlorotrimethylsilane (8 mL, 60 mmol) in tetrahydrofuran (10 mL) during 30 min. Upon completion of this addition, the ice bath was removed and stirring was continued overnight at room temperature. Water (30 mL) was added and the separated organic layer was extracted with 1 M sodium hydroxide solution (3 × 70 mL). The combined alkaline layers were cooled in ice, acidified with 10% hydrochloric acid, and extracted with ether (3 × 100 mL). The combined ether extracts were washed with brine (100 mL), dried, and evaporated to leave an oil (1.9 g) which crystallized upon trituration with hexane. Three recrystallizations from hexane afforded pure **2** (1.3 g, 21%) as fine white needles: mp 199–200 °C; IR (KBr, cm<sup>-1</sup>) 3430, 3090, 3065, 2965, 1695, 845, 710; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.56–6.95 (m, 11 H), 2.17 (d, *J* = 4.5 Hz, 1 H), 1.69 (d, *J* = 4.5 Hz, 1 H), -0.16 (s, 9 H).

Anal. Calcd for C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>Si: C, 73.50; H, 7.14. Found: C, 73.63; H, 7.08.

**Resolution of 2.** A hot solution of *l*-cinchonidine (3.27 g, 0.011 mol) in ethanol (50 mL) was added to a solution of **2** (3.43 g, 0.011 mol) in acetone (25 mL) and allowed to stand in a refrigerator. Fractional crystallization in a mixed acetone-ethanol (v/v 5:1) solvent system eventually gave diastereomerically pure salt (1.5 g) which exhibited  $[\alpha]^{22}_D -61.8^\circ$  (c 2.6, CH<sub>2</sub>Cl<sub>2</sub>).

A solution of this material (0.79 g) in dichloromethane (100 mL) was washed with 5% hydrochloric acid (2 × 40 mL) and the aqueous layers were extracted with dichloromethane (30 mL). The combined organic phases were dried and evaporated to give white crystals of (-)-(*R*)-**3**, mp 179–180 °C,  $[\alpha]^{22}_D -49.2^\circ$  (c 1.5, C<sub>2</sub>H<sub>5</sub>OH).

**(-)-(*R*)-2,2-Diphenyl-1-(hydroxymethyl)-1-(trimethylsilyl)cyclopropane (4).** A cold (0 °C) solution of (-)-(*R*)-**3** ( $[\alpha]^{22}_D -49.0^\circ$ , 1.0 g, 3.2 mmol) in ether (50 mL) was treated with a slight excess of diazomethane in ether. Solvent evaporation and recrystallization from hexane gave 1.1 g (100%) of the (-)-(*R*) methyl ester as colorless crystals: mp 114–115 °C;  $[\alpha]^{22.5}_D -29.6^\circ$  (c 5.0, CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr, cm<sup>-1</sup>) 1720; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.5–7.0 (m, 10 H), 3.38 (s, 3 H), 2.19 (d, *J* = 4.5 Hz, 1 H), 1.91 (d, *J* = 4.5 Hz, 1 H), -0.14 (s, 9 H).

A cold (0 °C) stirred suspension of lithium aluminum hydride (0.47 g, 12.4 mmol) in anhydrous ether (10 mL) was treated dropwise with a solution of (-)-(*R*) methyl ester (1.0 g, 3.08 mmol) in the same solvent (12 mL). After being stirred for 6 h at room temperature, the reaction mixture was treated with 10% sodium hydroxide solution (1.5 mL), filtered to remove the precipitated salts, and dried to give 0.83 g (91%) of (-)-(*R*)-**4** as a colorless oil:  $[\alpha]^{22.5}_D -61.1^\circ$  (c 1.66, C<sub>2</sub>H<sub>5</sub>OH); IR

(32) Further recrystallization of the cinchonidine salt led to no additional change in optical rotation.

(33) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147; **1965**, *43*, 2704.

(34) Kawamura, T.; Tsumura, M.; Yokomichi, Y.; Yonezawa, T. *J. Am. Chem. Soc.* **1977**, *99*, 8251.

(35) Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625.

(36) Pauling, L. *J. Chem. Phys.* **1969**, *51*, 2767.

(37) This analysis, similar to that given in ref 13c, goes contrary to the Dewar hypothesis which argues that substituent electronegativity is not the factor which accounts for configurational stability in free radicals: Dewar, M. J. S.; Shanshal, M. *J. Am. Chem. Soc.* **1969**, *91*, 3654. Bingham, R. C.; Dewar, M. J. S. *Ibid.* **1973**, *95*, 7180, 7182.

(38) Cram, D. J.; Langemann, A.; Allinger, J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 5740.

(neat,  $\text{cm}^{-1}$ ) 3600;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.6–7.0 (m, 10 H), 3.81 (d,  $J = 11.5$  Hz, 1 H), 3.03 (d,  $J = 11.5$  Hz, 1 H), 1.39 (d,  $J = 4.0$  Hz, 1 H), 1.32 (br s, 1 H), 1.19 (d,  $J = 4.0$  Hz, 1 H),  $-0.16$  (s, 9 H).

(-)-(R)-2,2-Diphenyl-1-methyl-1-(trimethylsilyl)cyclopropane (5). **A. Tosylation and Hydride Reduction of (-)-(R)-4.** A cold ( $0^\circ\text{C}$ ) solution of (-)-(R)-4,  $[\alpha]^{22.5}_{\text{D}} -21.9$  ( $c$  0.012,  $\text{CH}_2\text{Cl}_2$ ), in dry tetrahydrofuran (6 mL) was treated sequentially with *n*-butyllithium (1.5 mL of 1.4 M in hexane, 2.1 mmol) and *p*-toluenesulfonyl chloride (0.42 g, 2.2 mmol) dissolved in tetrahydrofuran (5 mL). The reaction mixture was stirred overnight, treated with saturated ammonium chloride solution (2.5 mL), and filtered. This solution was added directly to a cold ( $0^\circ\text{C}$ ), stirred slurry of lithium aluminum hydride (0.30 g, 7.9 mmol) in dry ether (4 mL). Stirring was continued overnight, at which point 10% sodium hydroxide solution (2.5 mL) was added, the precipitated salts were filtered off and rinsed with ether (2 mL), and the filtrate was washed with brine (5 mL) and dried. Solvent evaporation gave an oily product (0.15 g) which was purified by MPLC on silica gel (elution with 1% ethyl acetate in petroleum ether). There was isolated 0.11 g (35% overall) of (-)-(R)-5 as a colorless oil:  $[\alpha]^{22.5}_{\text{D}} -57.6^\circ$  ( $c$  1.27,  $\text{CHCl}_3$ ); IR (neat,  $\text{cm}^{-1}$ ) 2950, 1250, 705;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.4–6.9 (m, 10 H), 1.45 (d,  $J = 3.9$  Hz, 1 H), 1.03 (d,  $J = 3.9$  Hz, 1 H), 0.91 (s, 3 H),  $-0.24$  (s, 9 H);  $m/e$  ( $\text{M}^+$ ) calcd, 280.1647; obsd, 280.1648.

**B. Lithiation-Alkylation of (-)-(R)-6.** To a cold ( $-70^\circ\text{C}$ ) solution of (-)-(R)-6<sup>18</sup> (0.104 g, 0.36 mmol),  $[\alpha]^{22.5}_{\text{D}} -108.2^\circ$  ( $c$  0.015,  $\text{CHCl}_3$ ), was slowly added a pentane solution of *tert*-butyllithium (0.30 mL of 1.3 M, 0.39 mmol) via syringe. The reaction mixture was stirred for 20 min and chlorotrimethylsilane (0.05 mL, 0.39 mmol) was similarly introduced. After 1 h of stirring at  $0^\circ\text{C}$ , water (1 mL) was added, the organic layer was separated, and the aqueous phase was extracted with ether (10 mL). The combined organic layers were dried and evaporated to leave an oil which was purified by MPLC on silica gel (elution with 0.5% ethyl acetate in petroleum ether). There was obtained 0.034 g (33%) of (-)-(R)-5 as a colorless oil,  $[\alpha]^{22.5}_{\text{D}} -58.6^\circ$  ( $c$  0.69,  $\text{CHCl}_3$ ), whose IR and  $^1\text{H NMR}$  spectra proved identical with those of the silane isolated in A.

**1-Bromo-2,2-diphenyl-1-(trimethylsilyl)cyclopropane (9). A. Hunsdiecker Reaction with Red Mercuric Oxide in Refluxing Carbon Tetrachloride.** A hot, stirred solution of (-)-(R)-3 (0.20 g, 0.64 mmol),  $[\alpha]^{22.5}_{\text{D}} -53.5^\circ$  ( $c$  21.5,  $\text{CHCl}_3$ ), in carbon tetrachloride (6 mL) was treated sequentially with red mercuric oxide (0.10 g, 0.46 mmol) and a solution of bromine (0.12 g, 0.75 mmol) in the same solvent (2.5 mL). The reaction mixture was heated to reflux for 6 h, cooled, filtered (the solids were rinsed with carbon tetrachloride), and evaporated. MPLC purification of the product (silica gel, elution with 6% ethyl acetate in petroleum ether) gave 0.13 g (59%) of 9, mp 68–69  $^\circ\text{C}$ , which exhibited essentially no rotation in chloroform or ethanol: IR (KBr,  $\text{cm}^{-1}$ ) 1245, 850, 840, 710, 55;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.5–7.0 (m, 10 H), 1.92 (d,  $J = 5.3$  Hz, 1 H), 1.84 (d,  $J = 5.3$  Hz, 1 H),  $-0.08$  (s, 9 H).

Anal. Calcd for  $\text{C}_{18}\text{H}_{21}\text{BrSi}$ : C, 62.60; H, 6.13. Found: C, 62.60; H, 6.06.

**B. Hunsdiecker Reaction with Red Mercuric Oxide in Dichloromethane at  $0$ – $25^\circ\text{C}$ .** Treatment of (-)-(R)-3 (0.101 g, 0.323 mmol) in cold ( $0^\circ\text{C}$ ) dichloromethane (5 mL) with red mercuric oxide (0.050 g, 0.23 mmol) and bromine (0.02 mL, 0.39 mmol) was performed as above. The reaction mixture was stirred at  $0^\circ\text{C}$  for 40 min and at room temperature for 20 min before filtration. Solvent evaporation left an oil which was purified by MPLC (silica gel, elution with 4% ethyl acetate in petroleum ether) to give 0.022 g (19% of 9 which was again racemic).

**C. Action of Bromine on the Silver Salt 10.** A solution of (-)-(R)-3 (0.311 g, 1.0 mmol) in methanol (2 mL) was treated dropwise with aqueous potassium hydroxide solution until pH 9 was attained. An aqueous solution of silver nitrate (0.17 g) was added and the precipitated salt (10) was separated by centrifugation, washed twice with water, and dried over  $\text{P}_2\text{O}_5$  in an Abderhalden apparatus at  $70^\circ\text{C}$  for 24 h. The yield was 0.25 g (60%).

To a cold ( $0^\circ\text{C}$ ), stirred suspension of dry 10 in dry carbon tetrachloride (5 mL) was added dropwise a solution of bromine (0.12 g, 0.075 mmol) in the same solvent (5 mL) during 15 min. The reaction mixture was stirred for an additional 20 min, filtered, and evaporated. Purification in the prescribed manner afforded 0.09 g (43%) of essentially racemic 9.

(-)-(R)-2,2-Diphenyl-1-(trimethylsilyl)cyclopropanecarboxaldehyde (11). A mixture of (-)-(R)-4 (0.8 g, 2.7 mmol),  $[\alpha]^{22.5}_{\text{D}} -9.6^\circ$  ( $c$  1.66,  $\text{CHCl}_3$ ), activated manganese dioxide (2.3 g, 26 mmol), and dry dichloromethane (25 mL) was stirred at room temperature for 24 h. The insolubles were separated by filtration and washed with dichloromethane. The filtrates were evaporated to give white crystals which were purified by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether) to give 0.61 g (77%) of 11: mp 86–87  $^\circ\text{C}$  (from petroleum ether);  $[\alpha]^{22.5}_{\text{D}} -138^\circ$  ( $c$  2.37,  $\text{CHCl}_3$ ); IR (KBr,  $\text{cm}^{-1}$ ) 1695, 1685;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )

$\delta$  8.53 (s, 1 H), 7.4–7.0 (m, 10 H), 2.11 (d,  $J = 5.0$  Hz, 1 H), 1.97 (d,  $J = 5.0$  Hz, 1 H),  $-0.17$  (s, 9 H).

Anal. Calcd for  $\text{C}_{19}\text{H}_{22}\text{OSi}$ : C, 77.50; H, 7.53. Found: C, 77.37; H, 7.53.

(+)-(R)-1-Benzoyl-2,2-diphenyl-1-(trimethylsilyl)cyclopropane (12). A cold ( $0^\circ\text{C}$ ), magnetically stirred solution of (-)-(R)-11 (0.20 g, 0.68 mmol),  $[\alpha]^{22.5}_{\text{D}} -138^\circ$  ( $c$  2.37,  $\text{CHCl}_3$ ), in dry ether (10 mL) was treated dropwise with phenyllithium (1.8 mL of 2 M, 3.6 mmol) in ether-cyclohexane solution. After 1.5 h, water (0.5 mL) was added and the organic layer was dried and evaporated. The residual white solid was purified by MPLC (silica gel, elution with 5% ethyl acetate in petroleum ether) to give 0.23 g (90%) of alcohol: mp 154–156  $^\circ\text{C}$ ;  $[\alpha]^{22.5}_{\text{D}} +129^\circ$  ( $c$  0.86,  $\text{CHCl}_3$ ); IR (KBr,  $\text{cm}^{-1}$ ) 3570;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.9–7.0 (m, 15 H), 3.63 (br s, 1 H), 1.96 (d,  $J = 4.5$  Hz, 1 H), 1.62 (d,  $J = 4.5$  Hz, 1 H),  $-0.48$  (s, 9 H).

The above alcohol (0.196 g, 0.53 mmol) and activated manganese dioxide (0.70 g, 8.1 mmol) in dry dichloromethane (10 mL) were magnetically stirred for 20 h at room temperature. The insolubles were removed by filtration and rinsed with dichloromethane. The oily product obtained by solvent evaporation was purified by MPLC (silica gel, elution with 5% ethyl acetate in petroleum ether) to give 0.19 g (98%) of (+)-(R)-12 as a colorless solid: mp 98  $^\circ\text{C}$  (from petroleum ether);  $[\alpha]^{22.5}_{\text{D}} +135^\circ$  ( $c$  1.07,  $\text{CHCl}_3$ ); IR (neat,  $\text{cm}^{-1}$ ) 1660, 1655;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.8–6.9 (m, 15 H), 2.50 (d,  $J = 4.6$  Hz, 1 H), 1.86 (d,  $J = 4.6$  Hz, 1 H),  $-0.20$  (s, 9 H).

Anal. Calcd for  $\text{C}_{25}\text{H}_{26}\text{OSi}$ : C, 81.03; H, 7.07. Found: C, 80.85; H, 7.12.

(-)-(R)-2,2-Diphenyl-1-(trimethylsilyl)cyclopropane (13). A mixture of (+)-(R)-12 (0.0746 g, 0.20 mmol),  $[\alpha]^{22.5}_{\text{D}} +135^\circ$  ( $c$  1.97,  $\text{CHCl}_3$ ), and sodium amide (0.050 g, 1.3 mmol) in dry benzene (5 mL) was heated at the reflux temperature for 2 h and poured into cold water (10 mL). The aqueous layer was separated and extracted with ether. The combined organic phases were dried and evaporated to leave an oil which was purified by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). There was isolated 0.0146 g (27%) of (-)-(R)-13 as a colorless oil:  $[\alpha]^{22.5}_{\text{D}} -167^\circ$  ( $c$  1.46,  $\text{CHCl}_3$ ); IR (neat,  $\text{cm}^{-1}$ ) 1247, 832, 693;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.4–7.0 (m, 10 H), 1.46 (dd,  $J = 8.5$  and 5.5 Hz, 1 H), 1.17 (d,  $J = 10.5$  and 5.5 Hz, 1 H), 0.68 (X part of ABX,  $J = 10.5$  and 8.5 Hz, 1 H), 0.23 (s, 9 H).

Anal. Calcd for  $\text{C}_{18}\text{H}_{22}\text{Si}$ : C, 81.14; H, 8.32. Found: C, 81.12; H, 8.46.

( $\pm$ )-2,2-Diphenyl-1-(trimethylsilyl)cyclopropane (14). A mixture of racemic 9 (0.14 g, 0.41 mmol) and lithium aluminum hydride (0.085 g, 2.24 mmol) in dry ether (2 mL) was magnetically stirred at room temperature for 20 h. Potassium hydroxide solution (10%, 1 mL) was added and the precipitated salt were filtered and rinsed with ether. The combined filtrates were dried and evaporated to leave an oil that was purified by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). There was obtained 70 mg (50%) of starting bromide and 30 mg (56% corrected) of 14 whose spectra were identical with those of (-)-13 described above.

**Preparation and Resolution of *trans*-2,2-Diphenyl-3-(trimethylsilyl)cyclopropanecarboxylic Acid (15).** A solution of the methyl ester of ( $\pm$ )-15 (5.0 g, 15 mmol) and potassium hydroxide (1.13 g, 2.0 mmol) in ethanol (30 mL) was heated at reflux for 1.3 h. The solvent was evaporated and the residue was poured into water (100 mL). The mixture was extracted with ether (30 mL) and the aqueous layer was acidified with 1 N hydrochloric acid prior to ether extraction ( $2 \times 50$  mL). Following drying and evaporation of the combined organic layers, the carboxylic acid 15 was purified by recrystallization from hexane (1.6 g, 24%): mp 169–170  $^\circ\text{C}$ ; IR (KBr,  $\text{cm}^{-1}$ ) 3465, 3065, 1705;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  10.3 (br s, 1 H), 7.4–6.9 (m, 10 H), 2.52 (d,  $J = 7.5$  Hz, 1 H), 1.48 (d,  $J = 7.5$  Hz, 1 H),  $-0.20$  (s, 9 H).

A hot solution of 15 (0.92 g, 2.95 mmol) and *l*-cinchonidine (0.87 g, 2.96 mmol) in acetone containing a small amount of ethanol was allowed to stand at room temperature. Fractional recrystallization of the resulting crystals from acetone-ethanol eventually gave diastereomerically pure salt,  $[\alpha]^{22.5}_{\text{D}} -151^\circ$  ( $c$  1.18,  $\text{CHCl}_3$ ).

A solution of this salt in dichloromethane was shaken with 1 N hydrochloric acid. The aqueous phase was extracted with dichloromethane and the combined organic layers were dried and evaporated to give 16 as colorless crystals. The four crops which were obtained from various samples of the salt exhibited the following optical rotations:  $[\alpha]^{22.5}_{\text{D}} +285^\circ$  ( $c$  1.03,  $\text{CHCl}_3$ ),  $+234^\circ$  ( $c$  0.62,  $\text{CHCl}_3$ ),  $-165^\circ$  ( $c$  0.62,  $\text{CHCl}_3$ ),  $-280^\circ$  ( $c$  0.37,  $\text{CHCl}_3$ ).

(-)-1-(R)-3-(R)-1-Benzoyl-2,2-diphenyl-3-(trimethylsilyl)cyclopropane (18). To an ice-cold ( $0^\circ\text{C}$ ) solution of 16, (152 mg, 0.49 mmol),  $[\alpha]^{22.5}_{\text{D}} -165^\circ$ , in dry ether (10 mL) was added phenyllithium (0.5 mL of 2 M, 1.0 mmol). After 2 h, the reaction mixture was processed in the prescribed manner to give 79 mg (48%) of 18:  $[\alpha]^{22.5}_{\text{D}} -84^\circ$  ( $c$  0.48,

Table I. Crystallographic Details for (+)-17

formula	C <sub>29</sub> H <sub>40</sub> O <sub>2</sub> Si
M <sub>r</sub>	448.73
space group	P2 <sub>1</sub> -C <sub>2</sub> <sup>2</sup>
a, Å	6.792 (2)
b, Å	18.599 (4)
c, Å	10.794 (2)
β, deg	94.97 (2)
V, Å <sup>3</sup>	1358
Z	2
density (calcd), g/cm <sup>3</sup>	1.097
radiation	Mo Kα (λ(Kα <sub>1</sub> ) = 0.70926 Å, with graphite monochromator)
linear abs coeff, cm <sup>-1</sup>	1.03
temp	20 (1) °C
2θ limits	4° ≤ 2θ ≤ 55°
scan speed	1.0-24.0°/min
background time/scan time	0.5 s
scan range	1.0° below Kα <sub>1</sub> to 1.0° above Kα <sub>2</sub>
data collected	+h, +k, ±l
unique data	2485
unique data with F <sub>o</sub> <sup>2</sup> > 2σ(F <sub>o</sub> <sup>2</sup> )	1734
final number of variables	212
R(F)	0.064
F <sub>w</sub> (F)	0.055
error in observation of unit weight, e	1.94

CHCl<sub>3</sub>; IR (neat, cm<sup>-1</sup>) 1678, 1673; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.2-8.0 (m, 2 H), 7.7-7.0 (m, 13 H), 3.65 (d, J = 7.5 Hz, 1 H), 2.04 (d, J = 7.5 Hz, 1 H), -0.14 (s, 9 H). This material was not further purified.

**Haller-Bauer Cleavage of (-)-18.** A mixture of **18** (0.075 g, 0.20 mmol), [α]<sub>D</sub><sup>22.5</sup> -84°, sodium amide (0.050 g, 1.3 mmol), and dry benzene (4 mL) was heated at reflux for 20 h. Following the prescribed workup, there was isolated 0.011 g (20%) of **13**, [α]<sub>D</sub><sup>22.5</sup> -96° (c 1.06, CHCl<sub>3</sub>); the <sup>1</sup>H NMR spectrum was identical with those obtained with the samples of this silane prepared earlier.

**1-Menthyl (+)-1-(S)-3-(S)-2,2-Diphenyl-3-(trimethylsilyl)cyclopropanecarboxylate (17).** A mixture of **16** (0.092 g, 0.30 mmol), [α]<sub>D</sub><sup>22.5</sup> +285, and thionyl chloride (0.9 g, 7.6 mmol) was heated at reflux for 2 h and the excess thionyl chloride was removed in vacuo. The residual acid chloride was taken up in dry ether (6 mL) and added to a solution of *l*-menthol (0.076 g, 0.49 mmol) in the same solvent (7 mL). The reaction mixture was heated at reflux for 1.5 h, cooled, washed with water (10 mL), dried, and evaporated. MPLC on silica gel (elution with 8% ethyl acetate in petroleum ether) and recrystallization from methanol furnished **17** (0.074 g, 55%): mp 139-140 °C; [α]<sub>D</sub><sup>22.5</sup> +166° (c 0.95, CHCl<sub>3</sub>); IR (KBr, cm<sup>-1</sup>) 1729; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.5-6.8 (m, 10 H), 2.56 (d, J = 7.5 Hz, 1 H), 1.94-0.54 (series of m, 20 H), -0.16 (s, 9 H).

**X-ray Crystal Structure Analysis of 17.** Suitable crystals were grown from methanol and are clear, colorless, elongated rods. Preliminary film work indicated the systematic absences OkO with k = 2n+1, consistent with space groups P2<sub>1</sub> or P2<sub>1</sub>/m. Because of the known chiral nature of

the molecule, P2<sub>1</sub> was chosen as the correct space group. The crystal used for data collection was cut from a long rod and was approximately 0.06 × 0.39 × 0.62 mm<sup>3</sup> in size. The lattice parameters a = 6.792 (2) Å, b = 18.599 (4) Å, c = 10.794 (2) Å and β = 94.97 (2)° were determined at 20 °C from a least-squares fit of diffractometer setting angles for 15 reflections in the 2θ range 15°-21°.

Intensity data were collected by the θ-2θ scan technique on a Syntex P1 diffractometer using graphite monochromated Mo Kα radiation. Crystallographic details appear in Table I. Of the 2485 unique reflections measured, 1734 have F<sub>o</sub><sup>2</sup> > 2σ(F<sub>o</sub><sup>2</sup>) and were used in the full-matrix least-squares refinements based on F<sub>o</sub>.<sup>39</sup>

The structure was solved with MULTAN 80; twenty non-hydrogen atoms were easily located on the E-map. The remainder of the molecule was elucidated using standard structure factor and Fourier techniques. Isotropic refinement of the model with phenyl rings treated as rigid groups (C-O v 1.395 Å) converged to an R index of 0.108. After a cycle of anisotropic refinement, hydrogen atoms appeared on difference electron density maps and were added as fixed contributions to the structure factors with C-H = 0.95 Å and B<sub>H</sub> = B<sub>C(iso)</sub> + 1.0 Å<sup>2</sup>. The two cyclopropyl ring hydrogens were allowed to refine. The final refinement cycle with anisotropic thermal parameters for the non-hydrogen atoms, isotropic rigid body refinement for both phenyl rings, and isotropic refinement for the cyclopropyl ring hydrogens yielded an R index of 0.064 and an R<sub>w</sub> index of 0.055 using 1734 measurements and 212 variables. The final difference electron density map was featureless with a maximum peak height of 0.53 e Å<sup>-3</sup>.

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**Registry No.** (±)-1, 88082-47-7; (±)-2, 88035-72-7; (-)-(R)-3, 88082-48-8; (-)-R-3-*l*-cinchonidine, 88082-53-5; (-)-(R)-3 methyl ester, 88035-81-8; (-)-(R)-4, 88035-73-8; (-)-(R)-5, 88035-74-9; (-)-(R)-6, 4542-82-9; (±)-9, 88056-68-2; (-)-(R)-10, 88082-49-9; (-)-(R)-11, 88035-75-0; (+)-(R)-12, 88035-76-1; **12-ol**, 88035-82-9; (-)-(R)-13, 88035-77-2; (±)-14, 88082-50-2; (±)-15, 88035-78-3; (±)-15 methyl ester, 88035-83-0; (+)-16, 88082-51-3; (-)-16, 88082-52-4; (+)-17, 88035-79-4; (-)-18, 88035-80-7; Me<sub>3</sub>SiCl, 75-77-4.

**Supplementary Material Available:** Stereodrawing of the unit cell (Figure 2) and tables of bond lengths and angles, least-squares planes, torsion angles, final positional and thermal parameters, and observed and calculated structure factors (Tables II-VIII) for (+)-17 (15 pages). Ordering information is given on any current masthead page.

(39) Sheldrick, G. M. "SHELX-76. Program for Crystal Structure Determination"; University Chemical Laboratory: Cambridge, England, 1976.

## Steric Effects of Bridgehead Carbons Which Are α to Carbonyls

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**Abstract:** The rates of alkaline hydrolysis of bi- and tricyclic bridgehead substituted esters varied inversely with the size of the bridge. Enthalpy and entropy of activation were found to be related to the flexibility of the systems. The kinetic results were compared with thermodynamic data and also with recent force-field calculations. It is suggested that base-catalyzed ester hydrolysis can be used to determine the effective size of alkyl substituents.

The first fairly successful evaluation of steric effects and their separation from electronic effects was proposed by Taft, using

acid- and base-catalyzed hydrolysis of esters and acid-catalyzed esterification of carboxylic acids.<sup>1,2</sup> Although the literature is