Stability and Oxidative Coupling of Chiral Vinyl- and Cyclopropylcopper Reagents. Formation of a Novel Dissymmetric Diene

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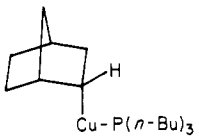
Chiral (*S*)-((4-methylcyclohexylidene)methyl)copper (**3**) and chiral (*S*)-(1-methyl-2,2-diphenylcyclopropyl)copper (**4**) have been prepared and shown to be optically stable. Oxidative coupling of (*R*)-**3** leads to the formation of an unusual chiral 1,3 diene having biaxial dissymmetry, (+)-(*aR*,*aR*)-bis(4-methylcyclohexylidene)ethane (**9**). The chiroptical properties of **9** are reported. The thermal and dioxygen reaction of (*S*)-(1-methyl-2,2-diphenylcyclopropyl)copper aggregate ((*S*)-**13**) leads to a variety of reaction products other than coupling to chiral and *meso*-bis(1-methyl-2,2-diphenylcyclopropane), (+)-(*R*,*R*)-**17** and (*R*,*S*)-**18**, respectively. The radical nature of the reaction is discussed.

Introduction

Organocopper reagents are versatile synthetic intermediates and their chemistry has been the subject of several reviews.[2] The most convenient method of preparation of these compounds is the reaction of an organolithium or Grignard reagent with a copper(I) salt such as in the reaction of an equimolar amount of an organolithium reagent with cuprous iodide. These compounds exist as aggregated clusters with structures which depend on the nature of the organic moiety and upon the presence of coordinating ligands.[3]

Reaction of 2 equiv of an organolithium reagent with 1 equiv of cuprous iodide results in the formation of a second type of organocopper reagent, the organocuprate or "ate complex".[4] Mixed cuprates can be prepared by the addition of 1 equiv of organolithium reagent to a preformed organocopper compound. The cuprates also appear to be aggregates in which the organic ligands are bound to a cluster of lithium and copper atoms. Moreover, there is no evidence for an equilibrium existing between organocuprates and their components, RLi and RCu.[5]

The stereochemical stability of organocopper reagents has received relatively little attention. Whitesides and co-workers[6] have shown that *endo*-2-norbornyl(tri-*n*-butylphosphine)copper(I) (**1**), phosphine-stabilized Cu–Csp^3



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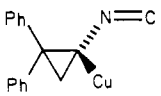
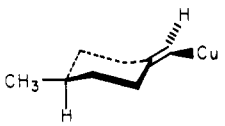
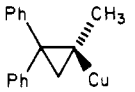


(*S*)-**2**



(*S*)-**3**

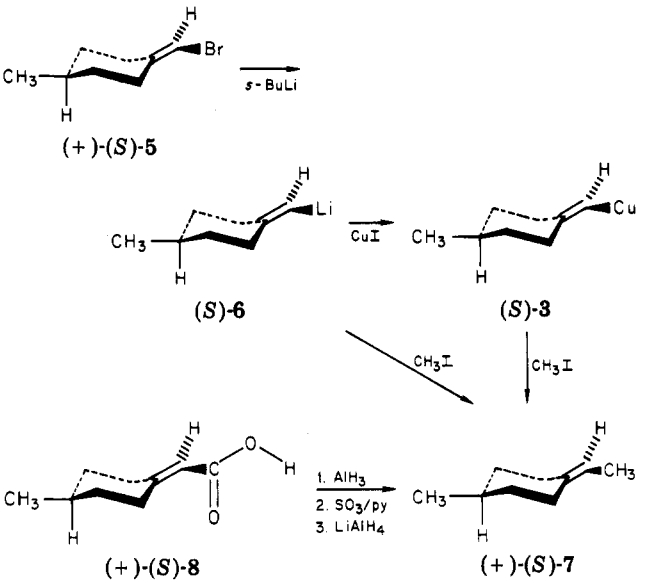
σ bond, is configurationally stable in ether at −30 °C. Recently, we have prepared an exceptionally stable chiral organocopper(I) compound, (1-isocyano-2,2-diphenylcyclopropyl)copper(I) (**2**), Cu–Csp$^{2.28}$ σ bond, which was shown to be stable at ambient temperature.[7] Vinylcopper(I) reagents,[8] Cu–Csp^2 σ bond, have also been shown to retain their configuration at −75 °C. Chiral vinylcopper reagent **3** has been prepared[9] and shown to be optically stable at −35 °C. In this article we report the results of our studies on the stability and oxidative coupling of chiral vinylcopper **3** and chiral cyclopropylcopper **4**.



(*S*)-**4**

Results and Discussion

Chiral Vinylcopper. Optically active (*S*)-((4-methylcyclohexylidene)methyl)copper(I) (**3**) was prepared from (+)-(*S*)-(4-methylcyclohexylidene)methyl bromide (**5**)



(1) This work was supported by a grant from the National Science Foundation.

(2) A. E. Jukes, *Adv. Organomet. Chem.*, **12**, 215 (1974); J. Normant, *Synthesis* 63 (1972); T. Kaufmann, *Angew. Chem., Int. Ed. Engl.*, **13**, 291 (1974); G. H. Posner, *Org. React.*, **22**, 253 (1974).

(3) H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **34**, 3615 (1969); G. Van Koten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.* 59 (1972).

(4) H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952).

(5) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

(6) G. M. Whitesides, J. San Fillippo, Jr., E. R. Stredronsky, and C. P. Casey, *J. Am. Chem. Soc.*, **91**, 6542 (1969).

(7) M. P. Periasamy and H. M. Walborsky, *J. Am. Chem. Soc.*, **97**, 5930 (1975); H. M. Walborsky and M. P. Periasamy, *J. Organomet. Chem.*, 179 (1979).

(8) (a) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Am. Chem. Soc.*, **93**, 1379 (1971); (b) G. M. Whitesides, J. San Fillippo, C. P. Casey, and E. J. Panek, *ibid.*, **89**, 5302 (1967); (c) J. F. Normant, G. Calmez, C. Chuit, and J. Villieras, *Bull. Chim. Soc. Fr.*, 1656 (1974); *J. Organomet. Chem.* **77**, 269 (1974); *ibid.*, 281 (1974); (d) F. Naf and P. Degen, *Helv. Chim. Acta*, **54**, 1939 (1971); (e) R. J. Anderson et al, *J. Am. Chem. Soc.*, **97**, 1197 (1975); (f) J. Klein and R. M. Turbel, *ibid.*, **81**, 6186 (1969).

(9) A preliminary report of part of this work has appeared, see R. B. Banks and H. M. Walborsky, *J. Am. Chem. Soc.*, **98**, 3732 (1976) and references cited therein.

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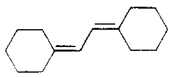
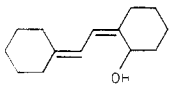
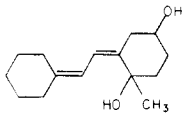
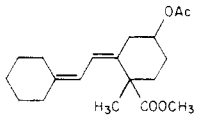
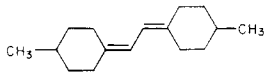
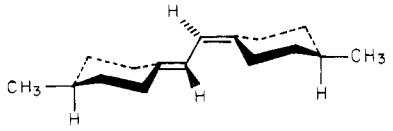
Table I. UV Spectra of Dicyclohexylideneethanes

compd	λ, nm	$10^{-3}\epsilon$	λ, nm	$10^{-3}\epsilon$	λ, nm 10	$10^{-3}\epsilon$
	241	31.6	250	38.1	259	26.5
	240	29.5	248	34.9	258	23.7
			245	16.4		
			246	18.8		
	242	31.8	250	38.8	259	27.5

whose absolute configuration has previously been established.[10] Halogen–metal exchange of **5** at −75 °C with *sec*-butyllithium, a reaction known to proceed with retention of configuration,[10,11] produced the corresponding (*S*)-((4-methylcyclohexylidene)methyl)lithium (**6**). The lithium reagent **6** was shown to be optically stable at temperatures below 0 °C.[10] Addition of 1 equiv of cuprous iodide to (*S*)-**6**, followed by stirring at −35 °C for 0.5 h, resulted in the formation of a dark suspension of (*S*)-**3**. With use of a modification of the Normant procedure,[8c] (*S*)-**3** was alkylated with methyl iodide to (+)-(*S*)-(4-methylcyclohexylidene)ethane (**7**). The lithium reagent (*S*)-**6** was also transformed to (+)-(*S*)-**7** by treatment with methyl iodide.

An authentic sample of (+)-(*S*)-**7** was prepared from (+)-(*S*)-4-methylcyclohexylideneacetic acid (**8**) using the Corey–Achiva procedure.[11] Since the absolute configuration and optical purity of **8** are known,[12] this enables one to establish the optical purity ($[\alpha]_{Hg}$ +17.7°) and absolute configuration of **7** as *S* with confidence, since the reactions used to effect this conversion would not be expected to lead to any racemization or inversion. With use of this datum, the conversion of **6** and **3** to **7** proceeds with 100% and 95% retention of optical activity or 100% and 98% retention of configuration.[13] Thus (S)-**3** represents the first example of a stable optically active vinylcopper compound.

Oxidative coupling of the optically active vinylcopper compound (*R*)-**3** resulted in the formation of a new optically active compound (+)-(*aR*,*aR*)-bis(4-methylcyclohexylidene)ethane. Passage of a stream of oxygen through



(+)-(*aR*,*aR*)-**9**

a THF suspension of the vinylcopper reagent (prepared from (−)-(*R*)-bromide, 94% optically pure) at −35 °C, followed by workup and purification of the crude product by chromatography on silver nitrate–silicic acid, gave a 30% yield of (+)-(*aR*,*aR*)-**9**, $[\alpha]^{25}_{Hg}$ +37.9 ± 0.8° (*c* 0.83, absolute EtOH). Diene **9** was characterized by its UV, IR, NMR, ORD, CD, and mass spectra. The UV, ORD, and CD spectra are shown in Figure 1. The optical purity of **9** has not been determined. However, there is no reason to believe that **9** is formed with significant loss of optical purity, since the vinylcopper reagent is configurationally stable at −35 °C and since *cis*- and *trans*-vinylcopper reagents couple with complete retention of configuration.[8] The diene is optically stable in ethanol solution for long periods of time at 0 °C.

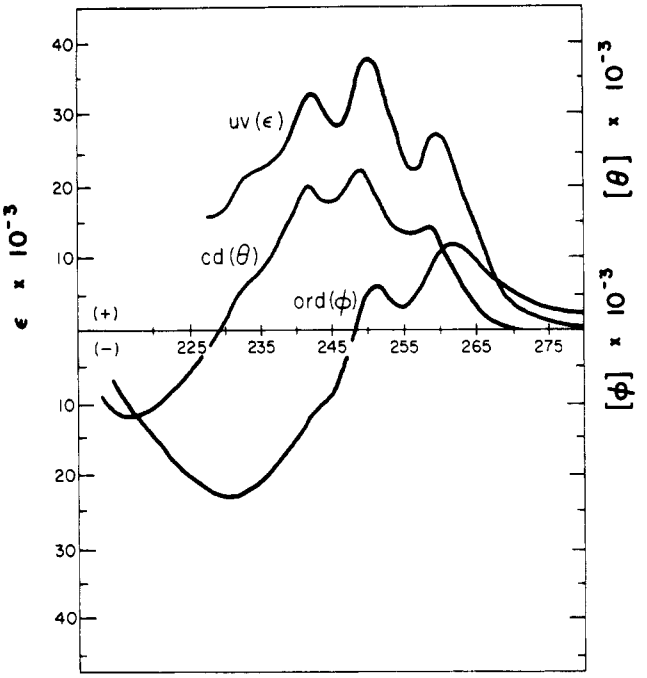


Figure 1. UV, CD, and ORD Spectra of (+)-(a*R*,a*R*)-bis(R-methylcyclohexylidene)ethane.

Optically active diene **9** arises from the stereospecific coupling of two dissymmetric axes of the same chirality and is assigned the absolute configuration (+)-(*aR*,*aR*). This assignment relates the configuration of **9** to that of (−)-(*R*)-**5** from which it is formed.

The ORD and CD spectra (Figure 1) of **9** show very intense Cotton effects associated with the conjugated diene chromophore. The structure of the CD maxima is analo-

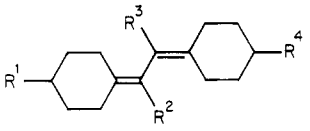
(10) H. M. Walborsky and R. B. Banks, *Bull. Soc. Chim. Belg.*, **89**, 849 (1980).
(11) E. J. Corey and K. Achiva, *J. Org. Chem.*, **34**, 3667 (1969).
(12) H. Gerlach, *Helv. Chim. Acta*, **49**, 1291 (1966).
(13) That **3** is alkylated with retention of configuration is based on the reasonable assumption that the conversion of **6** to **3** proceeds with retention. This is certainly the case when **6** is treated with $MgBr_2$.[10]

gous to that of the corresponding UV absorption. The UV absorption maxima of **9** are very similar to those observed for achiral dicyclohexylideneethanes (Table I).[14]

A conjugated diene is chiral if the diene unit is structurally or sterically distorted from planarity (skewed) or if there are other elements of dissymmetry in the molecule (nonskewed). Previous research has focused primarily on skewed dienes.[15] The chiroptical properties of such nonplanar dienes are characteristic of inherently dissymmetric chromophores—large molecular rotations and intense CD maxima paralleling intense UV absorption.[16] The signs of the Cotton effects of a large number of homo- and heteroannular *cisoid* and heteroannular *transoid* dienes have been related to the sense of twist of the diene moities.[17] Recently, the barriers to enantiomerization of skewed conformers of several cyclic and acyclic conjugated dienes have been determined by dynamic NMR measurement.[15b,18]

Relatively few investigations have been made of planar diene chromophores in dissymmetric environments. The CD spectra of *cis*- and *trans*-(*S*)-(+)-5-methyl-1,3-heptadiene show weak maxima associated with asymmetric perturbation of the symmetrical butadiene moiety.[19]

The chromophore of **9** fits between the extremes of the inherently dissymmetric and symmetric (asymmetrically substituted) butadiene. The dissymmetry of **9** arises from the combination of two chiral olefinic axes rather than from skewed or asymmetrically substituted double bonds. Therefore, **9** is the first member of a new class of dissymmetric conjugated dienes—the dicyclohexylideneethane derivatives, **10**. This family includes **9** as a special case in which the axes, a_1 and a_2, are structurally identical ($R^1 = R^4$, $R^2 = R^3$). Similar optically active dicycloalkylidenealkanes may be envisioned for other even-numbered ring systems.

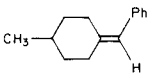
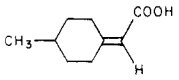
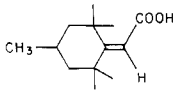
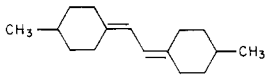


10

Suitable substituents, R^2 and R^3, of diene **10** should stabilize skewed rotamers with respect to the planar form. This would, therefore, introduce an additional element of chirality for this type of molecule. However, there is no evidence that **9** is sufficiently hindered to prevent rapid interconversion of the two skewed diastereomers.

Interpretation of the ORD and CD spectra of **9** is difficult since the diene chromophore of this molecule is novel.[20] The intense Cotton effects probably reflect the distortion of each double bond with respect to the attached cyclohexane rings rather than the twistedness of the diene chromophore itself.[21] In fact, the positve Cotton effects associated with the long wavelength absorption maxima of (*aR*,*aR*)-**9** correlate with the positive Cotton effects observed for similar cyclohexylidenealkane derivatives containing extended conjugation and having the same absolute configuration about the chiral olefinic axes (Table II).

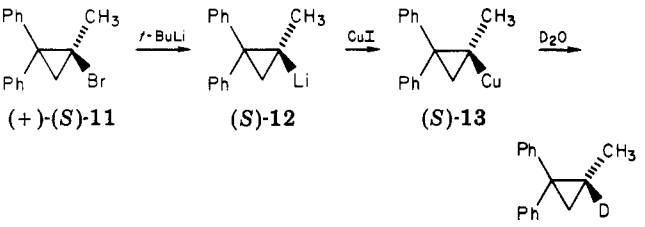
Table II. Observed Cotton Effects for Conjugated Cyclohexylidenealkanes

compd	configuration	cotton effect[a]	ref
	(−)-(*aR*)	+	21a, 22b
	(−)-(*aR*)	+	22a
	(−)-(*aR*)	+	22a
	(+)-(*aR*,*aR*)	+	this work

[a] For lowest energy absorption.

Chiral Cyclopropylcopper. We have recently reported the preparation of an unusually stable chiral copper(I) reagent, (1-isocyano-2,2-diphenylcyclopropyl)copper (**2**).[7] Since the isocyano substituent has been shown to have a stabilizing effect[23] on the cyclopropyl anion, it was not clear whether the stability of **2** was due to the isocyano group or to the cyclopropyl–copper σ bond. Therefore, a study of optically active cyclopropylcopper compounds without the isocyano substituent was undertaken for comparison with the vinylcopper and (isocyanocyclopropyl)copper reagents.

Chiral (+)-(*S*)-1-bromo-1-methyl-2,2-diphenylcyclopropane was converted to the corresponding lithium derivative (*S*)-**12** by metal–halogen exchange with *tert*-butyllithium in THF. Addition of 1 equiv of cuprous iodide to this cyclopropyllithium reagent resulted in the formation of a dark brown mixture. The reaction mixture was stirred at 0 °C for 1 h and then hydrolyzed with D_2O to give (−)-(*R*)-1-methyl-2,2-diphenylcyclopropane (83%). The



(+)-(*S*)-**11** (*S*)-**12** (*S*)-**13** (−)-(*R*)-**14**

(14) I. T. Harrison, B. Lythgoe, and S. Trippett, *J. Chem. Soc.*, 4016 (1955); O. Dimroth and H. Jonsson, *Chem. Ber.*, **71**, 2658 (1938); H. Booker, L. K. Evans, and A. E. Gilliam, *J. Chem. Soc.*, 1453 (1940); R. Burckhardt, *J. Chem. Soc.*, 10 (1940).

(15) (a) U. Weiss, H. Ziffer, and E. Charney, *Tetrahedron*, **21**, 3105 (1965); E. Charney, H. Ziffer, and U. Weiss, *ibid.*, 3121 (1965); E. Charney, *ibid.*, 3127 (1965); (b) L. W. Jelinski and E. F. Kiefer, *J. Am. Chem. Soc.*, **98**, 281 (1976); L. W. Jelinski and E. F. Kiefer *ibid.*, 282 (1976) and references cited therein.

(16) A. Moscowitz, Chapter 12 in "Optical Rotatory Dispersion: Applications to Organic Chemistry", C. Djerassi, Ed., McGraw-Hill, New York, 1960. A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

(17) A. W. Burgstahler, D. L. Boger, and N. E. Naik, *Tetrahedron*, **32**, 309 (1976); A. W. Burgstahler, L. O. Wiegel, and J. K. Gawronski, *J. Am. Chem. Soc.*, **98**, 3015 (1976); J. Gawronski and K. Gawronski, *J. Chem. Soc. Chem. Commun.*, 346 (1980); R. M. Moriarty, H. E. Paaren, U. Weiss, and W. B. Whalley, *J. Am. Chem. Soc.*, **101**, 6804 (1979).

(18) H. Bodecker, V. Jones, B. Kolb, A. Mannschrech, and G. Kobrich, *Chem. Ber.*, **108**, 3491 (1975) and references cited therein.

(19) A. DiCorato, *Gazz. Chim. Ital.*, **98**, 810 (1968).

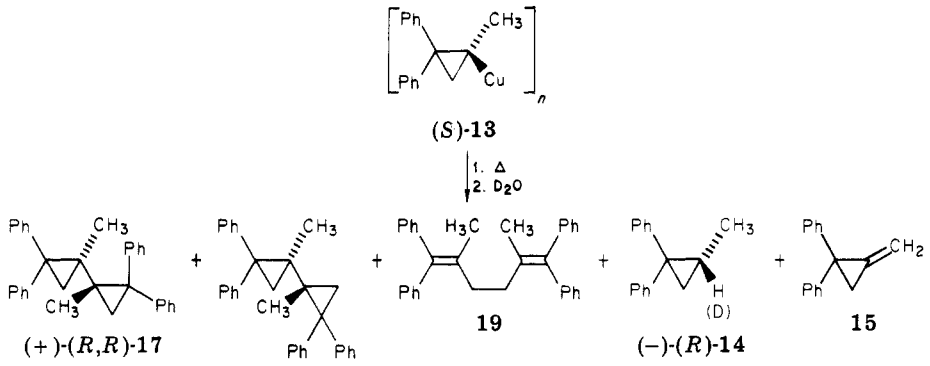
(20) Actually this chromophore is present in vitamin D_3 but has not been recognized as a chiral chromophore, and therefore their chiroptical properties have never been investigated. We have measured the CD spectra of a numer of isomers of 10,19-dihydro vitamin D_3 kindly supplied to us by Professor W. H. Okamura. We will report on them in a future publication.

(21) (a) J. H. Brewster and J. V. Privett, *J. Amer. Chem. Soc.*, **88**, 1419 (1966); (b) D. N. Kirk and R. J. Mullins, *J. Chem. Soc., Perkin Trans. 1*, 14 (1974) and references cited therein.

(22) (a) J. F. Arnett and H. M. Walborsky, *J. Org. Chem.*, **37**, 3678 (1972); (b) H. J. Bestmann and J. Lienart, *Angew. Chem., Int. Ed. Engl.*, **8**, 763 (1969).

(23) M. P. Periasamy and H. M. Walborsky, *J. Am. Chem. Soc.*, **99**, 2631 (1977).

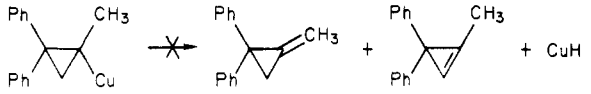
Scheme I



	(+)-(R,R)-17	(R,S)-18	19	(−)-(R)-14	15
$[\alpha]^{27}_{Hg}$, deg	+34.3	0		−80.7	
yield, %	31*	19	5	28	1

*27% (+)-(R,R) and 4% (−)-(S,S)

hydrocarbon (−)-(R)-14 was formed with retention of configuration (100% optically pure) and with 88% deuterium incorporation. It should be noted that although 13 has a copper(I) attached to a tertiary carbon atom, one



does not observe elimination of cuprous hydride under the conditions of the reaction since such an elimination would lead to highly strained products 15 and 16. The high retention of configuration (100%) observed and the stability toward elimination lead one to conclude that 13 is an extraordinarily stable Cu(I) species.

However, if after keeping 13 at 0 °C for 1 h one refluxes the THF solution for an additional 4 h, then 13 undergoes further reaction (Scheme I). The reaction mixture was hydrolyzed with D_2O before workup in order to detect any unreacted 13 or other organometallic intermediates.

As can be seen five products are formed in the thermal reaction of (S)-13 in the yields shown. The overall isolated material balance was 85%. Compounds 14, 15, 19, and the racemic modification of 17 have previously been characterized. They are products isolated from the reaction of 11 with magnesium metal, the Grignard formation reaction.[24] The R,R configuration has been assigned to 17 on the basis of the known propensity for copper reagents to couple with retention of configuration.[8] Compound 18 has been assigned the meso structure on the basis of the following data. It is optically inactive and gives a molecular ion of m/e 414 in the mass spectrum which is isomeric with 17. In the ^{1}H NMR spectrum it has two doublets for the H_A–H_B proton of the cyclopropane at 0.72 ppm (1 H) and at 1.33 ppm (1 H) each with a J = 5 Hz which is typical for this system. The methyl singlet is found at 1.13 ppm (3 H) and multiplets for the phenyl protons are observed between 6.8 and 7.3 ppm (10 H). The ^{13}C NMR shows six doublets and two singlets in the aromatic region (125–145 ppm) for the two different phenyl groups, a quartet for the methyl at 25.53 ppm, a triplet for the CH_2 of the cyclopropane at 24.77 ppm, a singlet at 32.61 ppm for the cyclopropyl carbon to which the methyl is attached, and a singlet for the cyclopropyl carbon which has two phenyl groups at 42.61 ppm. The simplicity of the NMR spectra, the molecular ion (EI) of m/e 414, and the observed 0 °C rotation are all consistent with the meso structure assigned to 18. The ^{1}H NMR and ^{13}C NMR spectra of 18 differ from 17 (see Experimental Section) so that 18 cannot be a racemic modification of 17.

Product analyses, including stereochemistry, lead one to the following mechanistic interpretation of the thermal reaction of $[(S)\text{-}13]_n$. Existing evidence indicates that $[R\text{–}Cu^I]_n$ exists in benzene as a tetramer (n = 4)[25–27] with tetrahedral configuration.[26,28] The copper triflate catalyzed thermal coupling of p-tolylcopper(I) in benzene leads exclusively to the formation of p,p'-bitolyl and no crossover coupling product with the solvent benzene.[27] This speaks strongly for an intramolecular coupling within the aggregate as does the stereospecific coupling observed in the thermal coupling of *cis*- and *trans*-propenylcopper(I).[8a] In the examples cited *free radicals* were excluded as intermediates in the thermal reaction although they have been postulated as intermediates in the thermolysis of neophyl(tri-n-butylphosphine)copper(I).[28]

Product analysis and stereochemical considerations lead one to postulate the mechanism depicted in Scheme II for the thermal decomposition of $[(S)\text{-}13]_n$. The aggregate $[(S)\text{-}13]_n$ is assumed to exist in solution where n = 2, 4, or 6. A mixture of aggregates probably exist in THF solution. The aggregates are stable at 0 °C for 1 h as judged by the deuteriolysis of $[(S)\text{-}13]_n$ which resulted in 88% deuterium incorporation in 14 and 100% retention of configuration. We view the aggregates $[(S)\text{-}13]_n$ as molecular species which exists in a solvent cage of THF. Upon thermolysis, a homolytic cleavage of two $R^{(S)}$–Cu bonds occurs with the formation of Cu^0 and the concomitant coupling, within the solvent cage (reaction a), of $R^{(S)}\cdot$ to (+)-(R,R)-17 with retention of configuration. If within the cage one of the $R^{(S)}\cdot$ rotates 180°, this would lead to formation of $R^{(R)}\cdot$ and coupling of the two radicals, $R^{(R)}\cdot$ and $R^{(S)}\cdot$, would produce *meso*-(R,S)-18 (reaction c). If two $R^{(S)}\cdot$ radicals rotate 180° and then couple, this would lead to the formation of (−)-(S,S)-17 (reaction b) which in combination with (+)-(R,R)-17 results in the production

(24) H. M. Walborsky and M. S. Aronoff, *J. Organomet. Chem.*, 51, 31 (1973) and references cited therein.

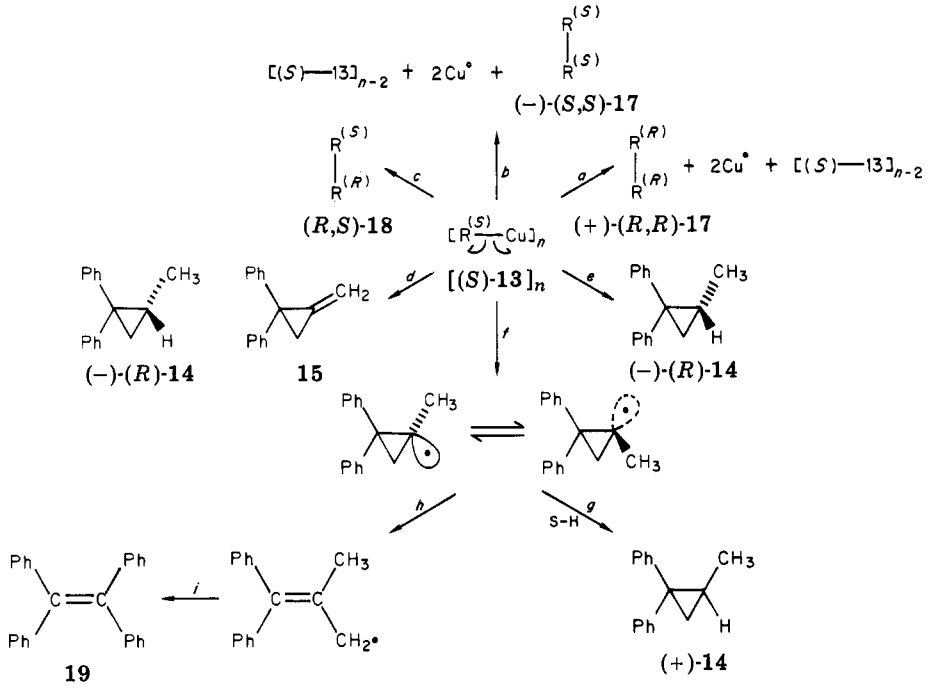
(25) J. A. Jarvis, B. T. Kilbourn, R. Pearce, and M. Lappert, *J. Chem. Soc., Chem. Commun.*, 475 (1973).

(26) A. Cairncross and W. A. Sheppard, *J. Am. Chem. Soc.*, 93, 247 (1971).

(27) G. Van Koten, J. T. B. H. Jastrzerbski, and J. G. Noltes, *J. Org. Chem.*, 42, 2047 (1977).

(28) G. M. Whitsides, E. J. Panek, and E. R. Stredronsky, *J. Am. chem. Soc.*, 94, 232 (1972); However, in a later publication[8a] they claimed radicals were not involved.

Scheme II. Thermal Decomposition of (*S*)-(1-Methyl-2,2-diphenylcyclopropyl)copper (R = 1-Methyl-2,2-diphenylcyclopropyl)



of the racemic compound (±)-(*R,R*/*S,S*)-17. That (±)-17 is a racemic compound can be seen from the fact that its melting point (184 °C)[24] is 19 °C higher than that of the pure enantiomer (165 °C). The racemic compound (±)-17 could not be separated in a pure state from the enantiomer. However, the racemic compound, (±)-17, proved to be more soluble in methanol than the enantiomer (+)-17 and the latter could be isolated by crystallization from methanol, mp 165 °C and $[\alpha]^{27}_{Hg}$ +46.4°. The mixture of (+)-17 and (±)-17 that remained in the mother liquors, mp 120–135 °C and $[\alpha]^{27}_{Hg}$ +8.2° had an NMR spectrum which was identical with that of pure (+)-17. Prior to recrystallization the mixture had a melting point of 152–154 °C and a $[\alpha]^{27}_{Hg}$ +34.3° which equates to 74% optical purity or that the mixture consists of 87% (*R,R*)-17 and 13% (*S,S*)-17 (74% (*R,R*)-17 and 26% racemic 17).

By itself, the formation of 17 takes on important significance. Its formation has never been observed in solution, only the products from reactions *g*, *h*, and *i* are observed. Also, the 1-methyl-2,2-diphenylcyclopropyl radical does not dimerize to 17 even in a cage reaction,[29a] but instead it follows the usual course expected for tertiary σ radicals, it disproportionates. The only other time that dimerization of this radical has been observed was when the radical was formed on a magnesium metal surface.[24] *Thus, the aggregates* [(*S*)-13]$_n$, *in their reactivity, resemble a surface reaction.*

The stereochemistry of reaction *e*, reaction with solvent cage wall, is not known but might be expected to proceed with overall retention of configuration. Reactions *a–e* are radical reactions which occur within the solvent cage, and the reaction of these radicals must occur, on a time scale, faster than diffusion of the radicals out of the cage,[30] $>10^{11}$ s^{-1}.

Reaction *f* is the diffusion of the radical from the solvent cage and into solution. The 1-methyl-2,2-diphenylcyclopropyl radical is a rapidly inverting (10^8 s^{-1}) σ radical.[31] In THF this free radical, generated from a precursor chiral diacyl peroxide, was shown to react with solvent to yield racemic (±)-14 and the dimer 19.[32] The latter, 19, is formed by the rearrangement of the cyclopropyl radical to the corresponding allyl radical which undergoes subsequent dimerization.[32] This same sequence of reactions, *g*, *h*, and *i*, is observed in the thermal reaction of [(*S*)-13]$_n$.

The hydrocarbon 14 formed in the thermal reaction of [(*S*)-13]$_n$ contained 27% deuterium. This represents the amount of [(*S*)-13]$_n$ that remained unreacted (~8% of total reaction) at the end of the reaction when the reaction mixture was quenched with D_2O. The reaction of [(*S*)-13]$_n$ with D_2O proceeds with 100% retention of configuration. Subtracting the amount of deuterio hydrocarbon with its retained configuration and the amount (3%) of 15 in the hydrocarbon mixture leads to a specific rotation for (−)-(*R*)-14, formed in reactions *d*, *e*, and *g*, of $[\alpha]^{27}_{Hg}$ −54.6° (optically pure 14, $[\alpha]^{27}_{Hg}$ −151°) or 36% optically pure. Perhaps fortuitously, this is comparable to the optical purity (~45%) observed for this radical forming hydrocarbon in a cage disproportion reaction.[29a] This would indicate that the solvent cage reactions *d* and *e* play a major role in the formation of 14.

Reaction of [(*S*)-13]$_n$ with Dioxygen. The oxidative coupling of [(*S*)-13]$_n$, by passing a stream of dioxygen through the reaction mixture, also leads to coupling[8] of the organic ligands but the reaction has interesting differences from that of the thermal coupling.

As can be seen from Table III a 60% yield of coupled product, (*R,R*)-17, with an optical purity of 93.5% (97% retention of configuration) is obtained when dioxygen with

(29) H. M. Walborsky and Jong-Chen Chen, *J. Am. Chem. Soc.*, **93**, 671 (1971). See also P. D. Bartlett and J. D. McBride, *Pure Appl. Chem.*, **15**, 89 (1967); K. R. Kopecky and T. Gillam, *Can. J. Chem.*, **47**, 2371 (1969); F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Am. Chem. Soc.*, **92**, 867 (1970).

(30) S. W. Benson, "Foundation of Chemical Kinetics", McGraw-Hill, New York, 1960.

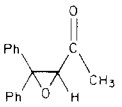
(31) For a detailed discussion of the cyclopropyl radical see H. M. Walborsky, *Tetrahedron*, **37**, 1625 (1981).

(32) H. M. Walborsky and Jong-Chen Chen, *J. Am. Chem. Soc.*, **92**, 7573 (1970).

(33) M. J. Jorgenson, *Tetrahedron Lett.*, 559 (1962).

(34) J. L. Webb, C. K. Mann, and H. M. Walborsky, *J. Am. Chem. Soc.*, **92**, 2042 (1970) report $[\alpha]^{25}_{Hg}$ 151° for optically pure 14.

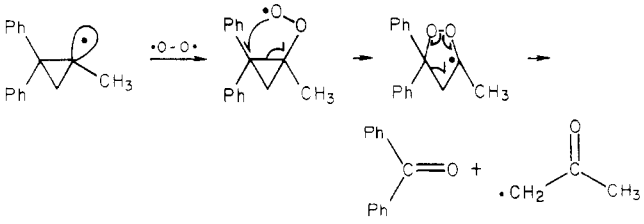
Table III. Products from the Reaction of $[(S)\text{-}13]_n$ with Dioxygen

reaction		[(−)-(R)-14 + 15]	(R,S)-18	(R,R)-17		
A[a]	yield, %	15.6	trace	29.0	27.6	
	$[\alpha]^{25}_{Hg}$ (OP, %)[f]	−120.1 (79.5)[e]		+39.2 (84.5)		
B[b]	yield, %	9.0	trace	60.7	5.3	4.5
	$[\alpha]^{25}_{Hg}$ (OP)[f]	−102.1 (67.6)[e]		+42.5 (91.6)		
C[c]	yield, %	20.1	6.9	14.2	~2	
	$[\alpha]^{25}_{Hg}$ (OP)[f]	−106.0 (70.2)[e]		+34.3 (73.9)		
D[d]	yield, %	14.1	trace	60.1	12.2	
	$[\alpha]^{25}_{Hg}$ (OP)[f]	−125.6 (83.2)[e]		+43.4 (93.5)		

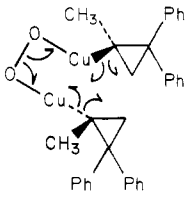
[a] T, 25 °C; O_2 flow rate, 50 mL/min. [b] T, −40 °C; O_2 flow rate, 180 mL/min. [c] T, −40 °C; O_2 flow rate, 50 mL/min. [d] T, −78 °C; O_2 flow rate, 100 mL/min. [e] Corrected for 0.2–3% 15 in mixture; $[\alpha]^{25}_{Hg}$ 151° for optically pure 14. [f] Optical purity.

a flow rate of 100 mL/min is passed through the reaction mixture at −78° C (reaction *D*). Increasing the temperature to −40 °C but increasing the flow rate of dioxygen to 180 mL/min gives a similar yield and stereochemical result (reaction *B*). Both the yield and optical purity of the coupled product is markedly reduced at higher temperatures and slower flow rate of dioxygen (reactions *A* and *C*). These data show that the best conditions for the stereospecific coupling reaction is low temperatures and a high flow rate of dioxygen. Moreover, oxidative coupling with dioxygen gives a higher yield and stereochemically purer coupled product than does the thermal coupling. This is emphasized by the fact that a 19% yield of *meso*-(*R*,*S*)-**18** is obtained in the thermal reaction whereas only traces are observed in the dioxygen reaction (reactions *A*, *B*, and *D*). The highest yield of (*R*,*S*)-**18**, and that only 6.9%, was observed in reaction *C*.

The hydrocarbon (−)-(*R*)-**14** and a small amount of **15** are also formed in the dioxygen coupling reaction, although in lower yield but with higher optical purity than in the thermal reaction. Significantly, no open dimeric product **19** is observed, indicating that the 1-methyl-2,2-diphenylcyclopropyl radical which escapes into solution is being very efficiently trapped by dioxygen. This would account for the lower yield and higher optical purity of hydrocarbon **14** obtained in the dioxygen reaction as compared to the thermal reaction since it would eliminate much of the racemic hydrocarbon (±)-**14** which would have been formed by reaction *f* in Scheme II. It is the dioxygen trapped radical which is probably responsible for the formation of benzophenone in the reaction.[35]



We view the reaction with dioxygen as proceeding by way of intermediate **20** which is formed by the reaction of dioxygen with aggregate $[(S)\text{-}13]_n$. The intermediate **20**, in solution, can then collapse by homolytic fission to form dimeric product (+)-(*R*,*R*)-**17**, disproportionate to hydrocarbons (−)-(*R*)-**14** and **15**, react with solvating portion of solvent to give (−)-(***R***)-**14** and (±)-**14**, or release radicals into solution to be trapped by dioxygen.



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It is also interesting to note that in one reaction ((*C*)) a small yield of an epoxy ketone was isolated. The origin of this product is currently under investigation.

Experimental Section

All melting points are uncorrected. Infrared spectra were measured with a Perkin-Elmer Model 257 grating infrared spectrophotometer. ^{1}H NMR spectra were obtained by using a Varian A-60 spectrometer. The spectra for measurement of deuterium content and ^{13}C were recorded with a Bruker 270-MHz spectrometer. Mass spectra were obtained with a A.E.I. Picker high-resolution mass spectrometer.

Optical rotations were measured at the 546.1-nm mercury line with a Bendix-Ericsson Model 987 automatic polarimeter with digital display attachment. Cell length was 0.4 dm. Error limits for rotations were calculated by multiplying the relative standard deviation by the specific rotation. The relative deviation was determined by dividing the standard deviation (0.002°) by the observed rotation.

The ORD and CD spectra were obtained with a Jasco Model recording spectrometer with 1.0-cm cells. UV spectra were obtained with a Cary 14 spectrophotometer with 1.0-cm cells.

GLPC analyses were conducted using an F&M Model 500 or Bendix Chroma-Lab Series 2100 gas chromatograph with thermal conductivity detectors. Analyses of 1-methyl-4-bromomethylenecyclohexane, 1-methyl-4-ethylidenecyclohexane, 1-methyl-4-methylenecyclohexane, and reaction mixtures containing these compounds were made with a 5 ft × $^1/_4$ in. copper column, packed with 20% Apiezon L on Chromasorb-P, on the Bendix chromatograph. Analyses of 1,2-bis(4-methylcyclohexylidene)ethane were carried out on the F&M Chromatograph using a 2 ft × $^1/_4$ in. copper column packed with silicone rubber. A 7 ft × $^1/_4$ in. copper column packed with 15% Lexan on Chromasorb P on the F&M chromatograph was used to analyze for methyl 4-methylcyclohexylideneacetate and 1-methyl-2,2-diphenylcyclopropane, HPLC was accomplished on a Waters Associates instrument equipped with a differential UV detector.

Optically Active ((4-Methylcyclohexylidene)methyl)copper ((*S*)-3) Reaction with Methyl Iodide. To a solution of (+)-(*S*)-(4-methylcyclohexylidene)methyl bromide (**5**), $[\alpha]^{25}_{Hg}$ +54.5° (*c* 1.0, absolute ethanol; 87% optically pure), 0.5 g in 10

(35) We wish to acknowledge a helpful discussion of this point with Professor Peter J. Wagner.

mL of THF at −75 °C, was added a solution (6 mL, 3.0 mmol) of 0.5 M *sec*-butyllithium in hexane. The mixture was allowed to stir at −75 °C for 2 h after complete addition. Cuprous iodide (0.6 g, 3.1 mmol) was then added and the mixture allowed to reach −35 °C and to stir for 45 min. During this time a dark black suspension was formed. HMPA (2.5 mL, freshly distilled from 13X molecular sieves) and 1.4 g of triethyl phosphite were added, and the mixture was allowed to sitr at −35 °C for 5 min. Methyl iodide (0.4 g, 2.7 mmol) was then added. After being stirred at −35 °C for an additional 15 min, the mixture was allowed to warm to room temperature and to stir for 12 h. The reaction was quenched with water and the ether layer separated. The ether extracts were washed eight times with water. It was found that triethyl phosphite could be completely removed by washing the extracts several times with dilute silver nitrate solution. The extracts were then washed with saturated sodium chloride and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave 0.25 g (76%) of a liquid. This liquid was chromatographed on 25 g of 25% silver nitrate–silicic acid, eluting first with 400 mL of pentane and then with 100 mL of 5% ether–hexane. The alkene was obtained in the ether fraction and after removal of solvent was further purified by bulb-to-bulb distillation (25 °C (2 torr)) to give 50 mg (15%) of (+)-(*S*)-(4-methylcyclohexylidene)ethane (7), $[\alpha]^{25}_{Hg}$ −14.7 ± 2.9° (*c* 0.16, $CHCl_3$; 83% optically pure; 95% optically pure based on starting bromide). The infrared and NMR spectra were identical with those of an authetic sample (vide infra).

Oxidative Coupling of (*S*)-((4-Methylcyclohexylidene)-methyl)copper (3). To a solution of 1 g (5.2 mmol) of (+)-(*S*)-5, $[\alpha]^{25}_{Hg}$ −58.3° (*c* 2.3, absolute ethanol; 94% optically pure), in 10 mL of THF at −75 °C was added a solution (10 mL, 5.5 mmol) of 0.55 M *sec*-butyllithium in hexane. After complete addition the mixture was allowed to stir at −75 °C for 1.5 h. Cuprous iodide (1.1 g, 5.2 mmol) was then added and the mixture allowed to warm to −35 °C and to stir for 30 min. A stream of oxygen was passed through the solution for 15–20 min at −35 to −40 °C. The mixture was then allowed to warm to room temperature and to stir for 4 h. The reaction mixture was hydrolyzed with water and filtered. The ether layer was washed three times with saturated ammonium chloride and two times with saturated sodium chloride and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave 0.47 g (83%) of oil which was chromatographed on 25 g of 25% silver nitrate–silicic acid, eluting first with 200 mL of pentane and then with 200 mL of 10% ether–pentane. From the ether–pentane fraction was obtained 0.2 g (30%) of an oil, $[\alpha]^{25}_{Hg}$ +37.9 ± 0.7° (*c* 0.63, absolute ethanol) which on the basis of its spectra was determined to be (*aR*,-*aR*)-bis(4-methylcyclohexylidene)ethane (9): ^1H NMR (CCl_4) δ 5.81 (s, 1 H), 0.85–2.9 (complex, 12 H); IR (CCl_4) 3040, 2920, 1620, 1455, 1390, 950 cm^{-1}; mass spectrum, *m/e* (relative intensity) 218 (100), 161 (40.5), 122 (45.3), 108 (47.6), 107 (57.3), 93 (82.9), 91 (64.6); exact mass of $M^{+\cdot}$ *m/e* 218.2028 ($C_{16}H_{26}$) measured, *m/e* 218.2034 ($C_{16}H_{26}$) calculated; UV (*c* 1.93 × 10^{-5} M, 95% ethanol) λ 259 (ε 27 500), 250 (38 820), 242 (31 860), 233 (sh (23 000); CD (*c* 9.53 × 10^{-5} M, 95% ethanol) $[\theta]_{270}$ 0, $[\theta]_{258.5}$ +14 560, $[\theta]_{249}$ +22 360, $[\theta]_{241.5}$ +20 176, $[\theta]_{234}$ +7280 (sh), $[\theta]_{217.5}$ −12 376, $[\theta]_{206}$ −6136 (sh); ORD (*c* 9.53 × 10^{-5} M, 95% ethanol) $[\phi]_{310}$ +1049, $[\phi]_{262}$ +1539, $[\phi]_{255}$ +3147, $[\phi]_{251}$ +6294, $[\phi]_{229}$ −23 078, $[\phi]_{210}$ −2078.

(+)-(*S*)-(4-Methylcyclohexylidene)ethanol. A modification of the procedure of Jorgensen[33] was used. To a slurry of 8.5 g (0.225 mol) of lithium aluminum hydride in 150 mL of anhydrous ether at 0 °C was added dropwise, with vigorous stirring, a solution of 10.0 g (0.075 mol) of aluminum chloride in 100 mL of ether. After being stirred an additional 1 h, a solution of 6.0 g (0.039 mol) of (+)-(*S*)-4-methylcyclohexylideneacetic acid, $[\alpha]^{25}_{Hg}$ +91.4° (*c* 0.64, absolute EtOH; 96.2% optically pure), in 50 mL of ether was added dropwise. After the mixture was stirred for 4 h, 16 mL of 5% sodium hydroxide was added slowly. The resulting lithium salts were filtered and washed with ether. The combined washings were dried ($MgSO_4$), and the solvent was removed in vacuo to give 4.8 g (88%) of (+)-(*S*)-2-(4-methylcyclohexylidene)ethanol: bp 78–79 °C (2 mm); $[\alpha]^{23}_{Hg}$ +7.6 ± 0.1° (*c* 3.9, $CHCl_3$); IR ($CHCl_3$) 3590 (nonbonded OH), 3410 (bonded OH), 1660 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 0.90 (d, *J* = 5 Hz), 0.90–2.7 (m, aliphatic), 3.6 (s, 1, hydroxyl), 4.1 (d, 2, *J* = 7 Hz, C=CHCH_2OH), 5.36 (t, 1, *J* = 7 Hz, C=C*H*CH_2OH); high-resolution mass spectrum *m/e* 140.1198 (calcd for $C_9H_{16}O$, *m/e* 140.1200).

(+)-(*S*)-(4-Methylcyclohexylidene)ethane (7). A modification of the procedure of Corey and Achiva was used.[11] A slurry of 2.2 g (0.015 mol) of (+)-(*S*)-2-(4-methylcyclohexylidene)ethanol (96.2% optically pure) and 3.18 g (0.02 mol) of sulfur trioxide–pyridine complex in 25 mL of THF was stirred at 0 °C for 20 h and at ambient temperature for 3 h. A solution of $LiAlH_4$ (0.09 mol) in THF was added at 0 °C, and then the mixture was stirred at 0 °C for 1 h. The mixture was cooled to 0 °C, 11 mL of 10% sodium hydroxide was added dropwise, and then 50 mL of ether was added. The salts were filtered and washed with additional ether. The combined filtrates were washed with dilute hydrochloric acid and dried ($CaSO_4$), and the solvent was removed in vacuo to yield 1.1 g of crude product. The product was chromatographed on a column of 40 g of alumina with elution by pentane and monitored by VPC on a 6 ft × $^1/_4$ in. 10% Apiezon L column to yield 0.3 g (15%) of (+)-(*S*)-(4-methylcyclohexylidene)ethane: bp 25–26 °C (2 mm); $[\alpha]^{24}_{Hg}$ +17.7 ± 0.2° (*c* 2.02, $CHCl_3$); this corresponds to a corrected rotation of +18.7 ± 0.2°; IR ($CHCl_3$) 3000–2850 (aliphatic), 1660 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 0.85 (d, *J* = 6 Hz, CH_3), 1.2–2.9 (m, cyclohexyl), 1.55 (d, *J* = 6 Hz, =CHCH_3), 5.0 (q, *J* = 6 Hz, =C*H*CH_3).

Anal. Calcd for C_9H_{16}: C 87.01; H 12.98. Found: C 87.02; H 12.97.

(+)-(*S*)-(4-Methylcyclohexylidene)ethane (7). To a solution of 0.50 g (2.7 mmol) of (+)-(*S*)-1-methyl-4-(bromomethylene)-cyclohexane, $[\alpha]^{24}_{Hg}$ +41.9 ± 0.2° (*c* 2.74, absolute EtOH; 67% optically pure), in dry THF at −76 °C was added 7.60 mL (5.32 mmol) of *tert*-butyllithium (1.21 M in pentane). The solution was stirred for 1.5 h, 2.14 g (15.0 mmol) of distilled methyl iodide was added, and the solution was allowed to warm to ambient temperature slowly. After 8 h, water was added, the aqueous layer extracted with ether, the combined ether layers were dried ($CaSO_4$), and the solvent was removed in vacuo to yield 0.3 g (91%) of (+)-(*S*)-(4-methylcyclohexylidene)ethane: bp 25–26 °C (2 mm); $[\alpha]^{24}_{Hg}$ +12.1 ± 0.1° (*c* 4.71, $CHCl_3$); this corresponds to a corrected rotation of +18.0 ± 0.1° for the optically pure alkene. The infrared and NMR spectra were identical with those of the sample previously reported.

Optically Active (1-Methyl-2,2-diphenylcyclopropyl)-copper (4). To a mixture of 0.5 g (1.75 mmol) of 1-methyl-1-bromo-2,2-diphenylcyclopropane, $[\alpha]^{25}_{Hg}$ +128.5° (*c* 0.72, $CHCl_3$; 98% optically pure)[34] in 25 mL of THF at −75 °C was added a solution (2.5 mL, 2.0 mmol) of 0.8 M *tert*-butyllithium in pentane. The mixture was stirred for 15 min, and then 0.35 g (1.75 mmol) of cuprous iodide was added. The mixture was then stirred at ice bath temperature for 1 h and hydrolyzed with D_2O. The ether extracts were washed with saturated sodium chloride and dried over anhydrous magnesium sulfate. Removal of solvent gave 0.3 g (83%) of a liquid which was shown by NMR and GLPC analysis to be 1-methyl-2,2-diphenylcyclopropane.[34] The hydrocarbon was purified by distillation (pot temperature 150–160 °C (2 torr): $[\alpha]^{25}_{Hg}$ +148.0 ± 1.2° (*c* 0.4, $CHCl_3$; 98% optically pure);[34] ^1H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.1 (m, 2 H), 2.2 (m, 0.22 H), 7.2 (m, 10 H). The corrected optical purity of the hydrocarbon was 100%, and the deuterium content determined by integration of the 270-MHz NMR spectrum was 88%.

Thermolysis of (*S*)-(1-Methyl-2,2-diphenylcyclopropyl)-copper (4). To a solution of 1.0 g (3.48 mmol) of (*S*)-(+)-1-methyl-2,2-diphenylcyclopropyl bromide ($[\alpha]^{27}_{Hg}$ +127.25 ± 0.70° (*c* 0.7, $CHCl_3$)) in 50 mL of dry THF at −78 °C under argon atmosphere was added 4.65 mL of 1.50 M *tert*-butyllithium over a period of 5 min. The resulting yellow solution was stirred for 15 min, and then 0.67 g (3.5 mmol) of dry cuprous iodide was added. A dark green suspension was obtained, and it was stirred for 15 min. The cooling bath was replaced by an ice bath, and the stirring continued for 1 h at 0 °C. The mixture was then gently refluxed for 4 h. The mixture was hydrolyzed by adding D_2O. The copper powder was filtered off, the THF solution was poured into water and extracted twice with hexane. Evaporation of the hexane solution gave 0.72 g of the crude product.

The crude product was separated into five components by using HPLC (porasil B, 8 ft × $^3/_8$ in.; heptane).

Component 1. A few milligrams were obtained, and it was not identified.

Component 2. This fraction was a mixture of 1-methyl-2,2-diphenylcyclopropane (14) and 1-deuterio-1-methyl-2,2-diphenylcyclopropane in 73:27 ratio (0.225 g, 29%), $[\alpha]^{27.5}_{Hg}$ −80.66 ± 0.63° (*c* 0.79, $CHCl_3$), corresponding to 53% optical purity of the hydrocarbons and 1-methylidene-2,2-diphenylcyclopropane (1%).

Component 3. A few milligrams were obtained and it was not identified.

Component 4. This component (0.100 g) was a mixture of 1,1,6,6-tetraphenyl-2,5-dimethylhexa-1,5-diene (19, 5%) and *meso*-bis(1-methyl-2,2-diphenylcyclopropane) (18, 19%). The mixture was reacted with *m*-chloroperbenzoic acid in CH_2CH_2 for 0.5 h. The nonpolar fraction of the crude product was separated by preparative TLC, and it was identified as the bis(cyclopropane): mp 160 °C; $[\alpha]^{27}_{Hg}$ 0.0°; IR (KBr) 3060–2850 (m), 1600, 1490, 1440, 1200–700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.72 (d, *J* = 5 Hz, 1 H), 1.13 (s, 3 H), 1.33 (d, *J* = 5 Hz, 1 H), 6.8–7.3 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 24.77 (t), 25.53 (q), 32.61 (s), 42.61 (s) 125.65 (d), 125.86 (d), 127.50 (d), 127.85 (d), 130.39 (d), 130.71 (d), 142.13 (s), 145.26 (s); mass spectrum (EI), *m/e* 414 ($M^{+\cdot}$).

Anal. Calcd for $C_{32}H_{30}$: C, 92.71; H, 7.29. Found: C, 92.59; H, 7.19.

Component 5. This fraction was (+)-(*R,R*)-bis(1-methyl-2,2-diphenylcyclopropane) (17) (0.22 g, 31%): mp 152–154 °C; $[\alpha]^{27}_{Hg}$ +34.30 ± 0.71° (*c* 0.71, $CHCl_3$); IR (KBr) 3060–2850 (m), 1600, 1580, 1490, 1380, 1100–700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ AB quartet centered at 0.70 (*J* = 5 Hz, 2 H), 1.23 (s, 3 H), 6.95–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 23.43 (q), 25.17 (t), 29.58 (s), 40.59 (s), 125.72 (d), 127.96 (d), 128.12 (d, 2 C), 129.70 (d), 130.06 (d), 144.11 (s), 144.68 (s). On crystallization from CH_3OH, the melting point increased (165 °C) and a maximum rotation of +46.41 ± 0.72° was obtained on the Hg line. The NMR spectrum did not change.

The sample, isolated by HPLC, mp 152–154 °C with $[\alpha]^{27}_{Hg}$ +34.3°, was recrystallized from methanol three times. Recrystallization gave a melting point of 165 °C $[\alpha]^{27}_{Hg}$ +46.4°, whereas the solid isolated from the mother liquors gave a melting point of 120-135 °C, [α] +8.2°, whose NMR spectrum was identical with the pure sample.

Anal. Calcd for $C_{32}H_{30}$: C, 92.71; H, 7.29. Found: C, 92.64; H, 7.39.

Reaction of (*S*)-(1-Methyl-2,2-diphenylcyclopropyl)copper (4) with Dioxygen. To a solution of 2.0 g (6.96 mmol) of (*S*)-(+)-1-methyl-2,2-diphenylcyclopropyl bromide ($[\alpha]^{27}_{Hg}$ +127.25 ± 0.70° (*c* 0.7, $CHCl_3$)) in 100 mL of dry THF at −78 °C (dry ice–acetone) under argon atmosphere was added 9.30 mL of 1.50 M *tert*-butyllithium over a period of 5–10 min. The resulting yellow solution was stirred for 15 min, and then 1.33 g (6.98 mmol) of dry cuprous iodide was added. A dark green suspension was obtained, and it was stirred for 15 min. The dry ice–acetone both was replaced by dry ice–acetonitrile bath (−42 °C), and a stream of oxygen (≃180 mL/min) was passed through the suspension. Within a few minutes a homogenous green solution was obtained. The passage of oxygen was continued at −42 °C for 4 h. The reaction mixture was quenched with D_2O and the poured into water and extracted with ether. The extract was washed with saturated NH_4Cl solution, dried over Na_2SO_4, filtered and evaporated to yield an oil.

The crude product was separated into four components by column chromatography (silica gel, hexane-ether).

Component 1. This was a mixture (0.134 g) of 1-methyl-2,2-diphenylcyclopropane (14) and 1-methylidene-2,2-diphenylcyclopropane (15) in 7.06% and 1.89% yields, respectively. The corrected rotation of cyclopropane (14), $[\alpha]^{27}_{Hg}$ −102.09 ± 0.64° (*c* 0.78, $CHCl_3$), corresponds to 67.6% optical purity. The sample did not contain deuterium.

Component 2. This was (+)-(*,R*)-bis(1-methyl-2,2-diphenylcyclopropane) (17) (0.875 g, 60.7%); $[\alpha]^{27}_{Hg}$ +42.22 ± 0.50° (*c* 1.0, $CHCl_3$).

Component 3. This was identified as benzophenone (0.067 g, 5.3%).

Component 4. This fraction (0.075 g) was identified as 1,1-diphenylbutenone epoxide by comparison of its spectral properties with those of an authentic sample.

Preparation of 1,1-Diphenylbutenone Epoxide. 1,1-**Diphenylbutenone**[36] (prepared from benzophenone and *N,N*-dimethylhydrazone of acetone[37]) was reduced with an excess of $NaBH_4$ in ethanol.

The reduction product was stirred with an excess of *m*-chloroperbenzoic acid in CH_2Cl_2 over aqueous Na_2CO_2 for 3 h. The mixture was diluted with ether and the aqueous phase removed. The organic phase was washed with sodium bisulfite, Na_2CO_3, and water, dried over Na_2SO_4, and evaporated to obtain a quantitative yield of the epoxy alcohol: ^1H NMR ($CDCl_3$) δ 1.23 (d, 3 H), 2.15 (OH), 4.30 (m, 1 H), 5.98 (d, 1 H), 6.80–7.30 (m, 10 H).

The epoxy alcohol (1.0 g) was stirred with 7 equiv of pyridinium dichromate[38] in DMF over night. The reaction mixture was poured into water and extracted with ether and the ether solution dried and evaporated to get an oil. The crude product was chromatographed to obtain the pure epoxy ketone: IR (film) 3120–2960 (multiplets), 1710 and 1600–625 (multiplets) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64 (s, 3 H), 3.77 (s, 1 H), 7.1–7.4 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 26.94 (q), 66.61 (s), 68.37 (d), 126.37 (d), 128.18 (d), 128.34 (d), 128.42 (d), 128.53 (d), 135.42 (s), 139.15 (s), 204.86 (s).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.73; H, 5.90.

Registry No. 3, 60164-98-9; 4, 80502-07-4; 5, 60164-94-5; 6, 77764-43-3; 7, 60164-99-0; 8, 28835-97-4; 9, 60164-97-8; 11, 6526-76-7; 12, 80502-08-05; 14, 14275-48-0; 14-*d*, 80502-09-6; (*R,R*)-17, 80502-10-9; (±)-17, 80558-51-6; 18, 80558-52-7; 19, 988-38-5; (+)-(*S*)-(4-methylcyclohexylidene)ethanol, 80502-11-0; 1,1-diphenylbutenone epoxide, 80502-12-1; 3-hydroxy-4,4-diphenylbutan-2-one, 14035-54-2; 1,1-diphenylbutenone, 837-66-1.

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