The proton nmr of 1,3-di(4-methylphenyl)-3-buten-1-one,[39] prepared by the method of Wayne and Adkins,[40] in the presence of a 0.12 mol ratio of $AgBF_4$ showed an aromatic multiplet at *ca.* 6.7 which did not appear in the simple AB system of complexed *p*-methylacetophenone.

Acknowledgment. Partial support of this work by the National Science Foundation and the Research Corporation is gratefully acknowledged. The authors would also like to thank Professor Carl O. Quicksall for helpful discussions.

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(39) H. Pines and J. Shabtai, *J. Org. Chem.*, **26**, 4220 (1961).

(40) W. Wayne and H. Adkins, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 367.

Generation and Utilization of Copper(I) Ate Complexes from Diastereomeric and Enantiomeric Alkylmercury Reagents[1]

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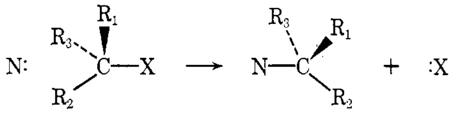
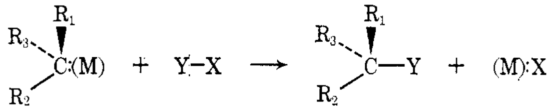
Abstract: Treatment of alkylmercuric halides in succession with 1 equiv of iodo(tri-*n*-butylphosphine)copper(I) and 3 equiv of *tert*-butyllithium at −78° in tetrahydrofuran results in formation of a reactive ate complex which incorporates the alkyl group originally bonded to mercury. The reactions of this alkyl group resemble those of a lithium dialkylcuprate: it can be alkylated with alkyl halides and coupled with a *tert*-butyl moiety by oxidation with nitrobenzene; it does not, however, undergo conjugate additions to α,β-unsaturated ketones. In certain instances, but not always, the overall conversion from alkylmercuric halide to product takes place with retention of configuration at the carbon originally bonded to mercury. The structure(s) of these ate complexes cannot be established from the available data, but qualitative evidence suggests that lithium, copper(I), and mercury(II) are all present in the metal core. Possible applications and limitations of these complexes in synthesis are briefly outlined.

The inversion of stereochemistry that characterizes SN2 displacement at carbon is the basis for many important methods of controlling stereochemistry in organic synthesis (eq 1). In principle, it should be possible to carry out stereoselective transformations at carbon using diastereomeric carbanions (or their functional equivalents) as nucleophiles (eq 2); these species would also be useful in mechanistic studies. In practice, difficulties in generating and utilizing the required nucleophilic species have prevented common use of procedures based on this principle. General methods for the synthesis of pure diastereomers of organolithium and magnesium species are not available,[3,4] and even in the special instances in which they have been prepared, only one of two diastereomers has been obtained.[5] Indeed, even if it were possible to generate diastereomerically pure *sec*-alkyllithium and -magnesium reagents, it is not clear that they would be more than marginally stable toward epimerization.[4–6]


(1)


(2)

In contrast, diastereomerically pure or enriched organometallic derivatives of a number of other metals—particularly mercury(II), tin(IV), and lead(IV)—have been prepared[7–9] and established not to epimerize readily once formed.[10] Unfortunately, organometallic derivatives of these metals are only weakly nucleophilic and of limited synthetic utility.

The work reported in this paper was directed toward developing methods for increasing the nucleophilic

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(1) Supported in part by the National Science Foundation, Grants GP-28586X and GP-14247, and by the International Copper Research Association.

(2) Texaco Predoctoral Fellow, 1971–1973.

(3) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3283 (1964); H. L. Goering and F. H. McCarron, *ibid.*, **80**, 2287 (1958), and references in each.

(4) Recent studies of the mechanism of conversion of alkyl bromides to alkylmagnesium and -lithium reagents by reaction with metal indicate that species resembling a radical in many of its properties are intermediates in these reactions: *cf.* H. M. Walborsky and M. S. Aronoff, *J. Organometal. Chem.*, **51**, 31 (1973); H. M. Walborsky and M. S. Aronoff, *ibid.*, **51**, 55 (1973); H. W. H. J. Bodewitz, C. Blomberg, and F. Bickelhaupt, *Tetrahedron*, **29**, 719 (1973); R. J. Rogers, H. L. Mitchell, Y. Fujiwara, and G. M. Whitesides, *J. Org. Chem.*, **39**, 857 (1974).

(5) F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **88**, 3437 (1966); W. H. Glaze and C. M. Selman, *J. Org. Chem.*, **33**, 1987 (1968); W. H. Glaze and C. M. Selman, *J. Organometal. Chem.*, **11**, P 3 (1968).

(6) G. M. Whitesides and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 4878 (1965); E. A. Pechtold, D. G. Adams, and G. Fraenkel, *J. Org. Chem.*, **36**, 1368 (1971); G. Fraenkel, C. E. Cottrell, and D. T. Dix, *J. Amer. Chem. Soc.*, **93**, 1704 (1971), and references in each.

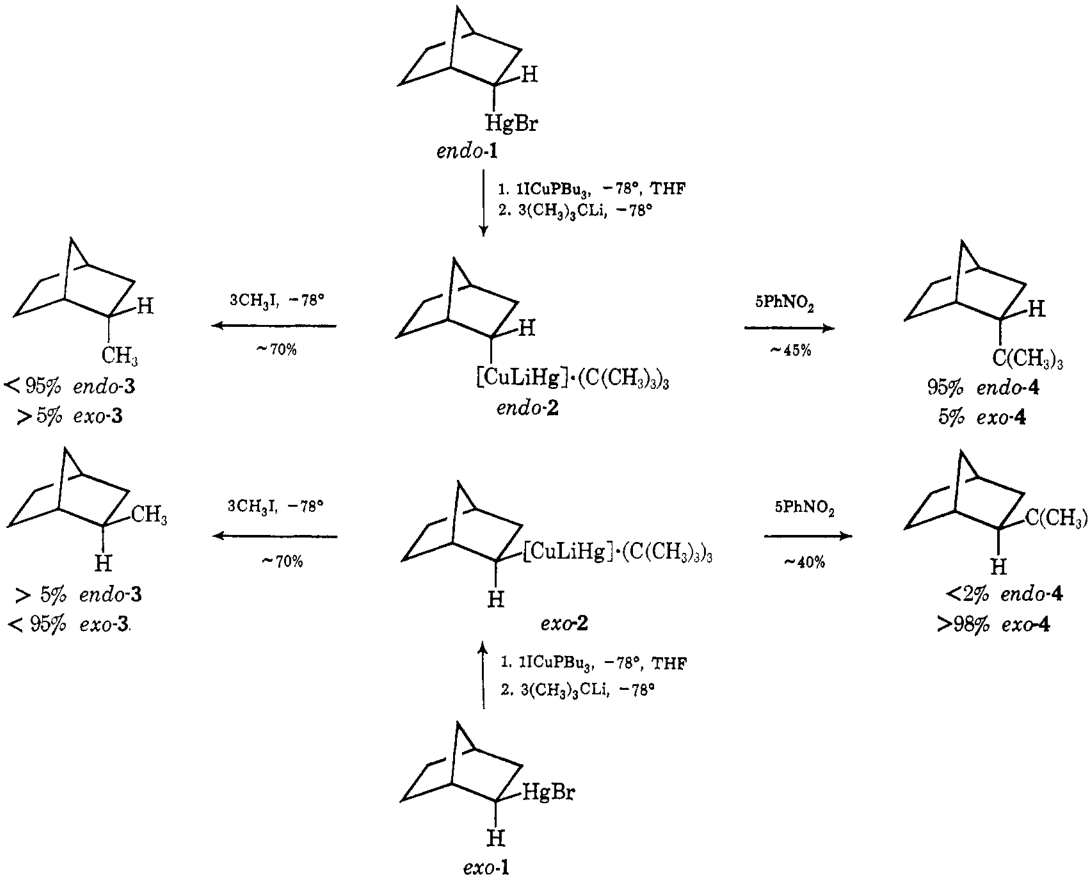
(7) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968.

(8) D. S. Matteson, *Organometal. Chem. Rev., Sect. A*, **4**, 263 (1969); D. Dodd and M. S. Johnson, *Chem. Commun.*, 571, 1371 (1971); G. S. Koermer, M. L. Hall, and T. G. Traylor, *J. Amer. Chem. Soc.*, **94**, 7205 (1972); H. G. Kuivila, J. L. Considine, and J. D. Kennedy, *ibid.*, **94**, 7206 (1972); O. A. Reutov, *et al.*, *Zh. Org. Khim.*, **5**, 19 (1969) [*Chem. Abstr.*, **70**, 87929b (1969)]; F. R. Jenson, J. J. Miller, S. J. Cristol, and R. S. Beckley, *J. Org. Chem.*, **37**, 4341 (1972).

(9) G. M. Whitesides and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, **92**, 6611 (1970); C. L. Hill and G. M. Whitesides, *ibid.*, **96**, 870 (1974).

(10) Although alkylmercuric reagents are stable toward epimerization once prepared, our own experience and a private communication from F. R. Jensen has emphasized the possibility of their epimerization in solution during recrystallization or chromatography. This epimerization apparently reflects a radical chain reaction initiated by small amounts of peroxides present in solvents or formed on exposure of alkylmercury compounds to oxygen.

Scheme I. Organomercury Compounds *endo*-**1** and *exo*-**1** Are Converted to a Copper Ate Complex and to Products with High Stereoselectivity



reactivity of one or more of the classes of organometallic substances capable of yielding diastereomerically or enantiomerically pure compounds, while at the same time retaining a useful degree of configurational stability at the carbon–metal bond. Effort has been concentrated on attempts to convert diastereomeric and enantiomeric organomercury compounds into copper(I) ate complexes[11] having reactivity[12] and configurational stability[13,14] similar to that of lithium diorganocuprates. This effort has been partially successful: certain organomercury reagents have been converted with useful stereoselectivity into copper(I) ate complexes having adequate reactivity for use in synthesis. Others, however, epimerize partially or completely during these transformations, or generate ate complexes of low reactivity. These studies suggest correlations between structural features in the starting organomercury reagents and the synthetic utility of the derived copper ate complexes, and provide qualitative information concerning a new and potentially valuable class of copper ate complexes.

Results

Initial experiments were carried out using *endo*- and *exo*-2-norbornylmercuric bromide (**1**) because lithium alkyl(*endo*-2-norbornyl)cuprates had previously been demonstrated to retain stereochemistry at the carbon–metal bond for long periods of time.[13,14] In a typical experiment, a tetrahydrofuran solution containing 1 mmol of *endo*-**1** was treated with 1 equiv of iodo(tri-*n*-butylphosphine)copper(I) at −78°, and then with 3.6 mmol of *tert*-butyllithium. The nature of the organometallic species present in the resulting solution has not been defined in detail; for convenience we will refer to them simply as *exo*- and *endo*-**2**. The representation used for **2** in Scheme I, R[CuLiHg]·(C(CH$_3$)$_3$)$_3$, should be taken to refer to the composition of the solution rather than to the structure of the complex, although qualitative evidence suggests that all three metals are incorporated into a common cluster in these ate complexes (*vide infra*).

Addition of methyl iodide (3 mmol) to the light yellow solution of *endo*-**2**, reaction of the resulting mixture for 30 min at −78°, and conventional work-up yielded 79% of 2-methylbornane (**3**, 95% endo, 5% exo) as determined by glpc analysis; oxidation of *endo*-**2** with an excess of nitrobenzene at −78° yielded ~40% of *endo*-2-*tert*-butylnorbornane (**4**, 95% endo, 5% exo). These and parallel results obtained starting with *exo*-**1** are outlined in Scheme I. Neither the yield nor the stereochemical purity of the products varied significantly with the proportions of reagents used, provided that RHgBr:ICuPEu$_3$:(CH$_3$)$_3$CLi is 1:1:3. If the transmetalation between **1** and *tert*-butyllithium is carried out before addition of ICuPBu$_3$, the products obtained from the resulting **2** are extensively epimerized.[15]

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[11] G. Wittig, *Quart. Rev., Chem. Soc.*, **20**, 191 (1966); W. Tochtermann, *Angew. Chem., Int. Ed. Engl.*, **5**, 351 (1966).

[12] J. F. Normant, *Synthesis*, 63 (1972); G. H. Posner, *Org. React.*, **19**, 1 (1972); G. Bähr and P. Burba in "Methoden der organischen Chemie," 4th ed, 13/1, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, Germany, 1970, pp 731–761.

[13] G. M. Whitesides, J. San Filippo, Jr., E. R. Stedronsky, and C. P. Casey, *J. Amer. Chem. Soc.*, **91**, 6542 (1969).

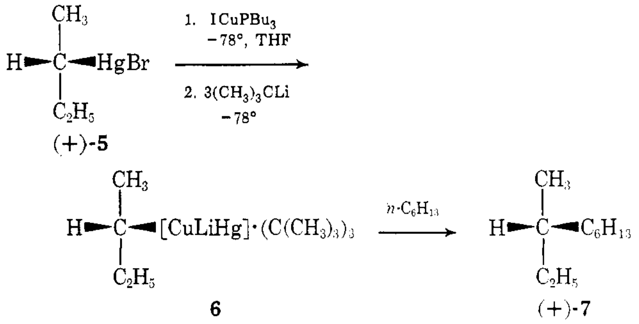
[14] G. M. Whitesides and P. E. Kendall, *J. Org. Chem.*, **37**, 3718 (1972).

Several qualitative observations concerning solutions of **2** indicate that this solution does not contain either norbornylmercury(II) halide, -(tri-*n*-butylphosphine)-copper(I), or -lithium in appreciable concentration, and that it also does not contain lithium (*tert*-butyl)(norbornyl)cuprate: First, **2** does not react with ketones under conditions that would result in rapid consumption of isopropyllithium or 2-norbornylmagnesium bromide. The thermal stability of **2** in THF solution (*ca.* 2 hr at 25°) is inconsistent with the thermal instability of 2-norbornyl(tri-*n*-butylphosphine)copper(I) and also with the reactivity of most secondary alkyllithium reagents toward THF. The facile conversion of **2** to **3** by reaction with methyl iodide, and of **2** to **4** with nitrobenzene, is incompatible with formulations of **2** as either 2-norbornylmercuric halide, bis-2-norbornylmercury, or 2-norbornyl(tri-*n*-butylphosphine)copper(I). The failure of **2** to add to mesityl oxide establishes that it is not simply an ate complex between 2-norbornyl(tri-*n*-butylphosphine)copper(I) and *tert*-butyllithium.[14] The simplest interpretation of all of these data is that **2** is a ternary ate complex containing copper(I), mercury(II), and lithium. The number of atoms of each metal in the cluster (if indeed there is only one type of cluster present), the disposition of norbornyl and *tert*-butyl groups on its surface, and the extent to which tri-*n*-butylphosphine and iodine ion are associated with the cluster are all unknown.

Efforts to substitute *sec*-butyllithium, isopropyllithium, *n*-butyllithium, or phenyllithium for *tert*-butyllithium in the preparation of **2** were not successful: in no instance was an ate complex obtained which was capable of transferring the norbornyl group in either alkylations or in oxidative couplings. This observation does not necessarily mean that no ate complex was formed on mixing **1**, $ICuPBu_3$, and these organolithium reagents, but only that if an ate complex is formed, it reacts by transfer of the alkyl group originally bonded to lithium, rather than the norbornyl group, with high selectivity.[16,17]

The transformations in Scheme I establish that it is possible to convert one particular type of secondary organomercury compound, **1**, to a reactive copper(I) ate complex, and to induce this ate complex to undergo certain types of reactions with high stereoselectivity. It is not evident, however, that stereochemical results obtained using the 2-norbornyl moiety are necessarily typical of other secondary organic groups. The *sec*-butyl group lacks the structural peculiarities associated with the 2-norbornyl moiety, and *sec*-butylmercuric bromide (**5**) has been resolved;[18,19] thus, the *sec*-butyl analog of **2** seemed to provide a compound that would give some indication of the generality of the stereochemical results obtained with **1**. When enantiomerically enriched (+)-*sec*-butylmercuric bromide was treated with $ICuPBu_3$ and *tert*-butyllithium using conditions similar to those employed with **1**, an ate complex, **6**, was formed which had reactivity similar to that of **2**.

The reaction of enantiomerically enriched **6** with 1-iodohexane was chosen for stereochemical examination. The product of this reaction, 3-methylnonane (**7**), is



stereochemically stable under the reaction conditions, and also under a rigorous work-up procedure designed to eliminate optically active impurities (see Experimental Section). In addition, the absolute configurations of (+)-**5**[18,19] and (+)-**7**[20] are both *S;* thus, the stereochemistry of the product and starting material can be related directly. The stereochemistry observed during conversions of (+)-**5** (*ca.* 33% enantiomeric excess) to (+)-**7** *via* **6** is summarized in Table I.

Table I. Conversion of (*S*)-(+)-3-*sec*-Butylmercuric Bromide (**5**) to (*S*)-(+)-3-Methylnonane (**7**)[a]

Reaction temp, °C	Equilibration[b] time for **6**, min	% stereo-selectivity[c] **5** → **7**	Yield, %[d]
−78[e]	60	57	25
−78[e,f]	300	58	25
−78	10	68	25
−78	60	71	25
−117	15	75	15

[a] These reactions were run with **5** having 32.8% enantiomeric excess (ee). [b] Equilibration time represents the time the complex **6** was allowed to stir at the indicated reaction temperature, before addition of 1-iodohexane. [c] % stereoselectivity is defined as [ee (**5**) − ee (**7**)]/ee (**5**). [d] These represent approximate isolated yields based on starting **5**. Yields assayed by glpc before work-up were *ca.* 45–50%. The work-up procedure used was specifically designed to eliminate possible contamination with optically active impurities, rather than to optimize yields. [e] The specially constructed apparatus described in the Experimental Section was not used in this experiment. As a consequence, addition of *tert*-butyllithium to the reaction mixture resulted in at least a 20–30° exotherm. [f] This reaction was run in the presence of 5 equiv of added HMPA.

The stereoselectivity of the overall conversion of **5** to **7** is lower than that of the corresponding reactions of the analogous 2-norbornyl ate complex **2**.[21] The loss

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(15) This epimerization may reflect formation of 2-norbornyllithium. *sec*-Butyllithium appears to invert rapidly on a chemical time scale: D. Y. Curtin and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **84**, 1967 (1962).

(16) A similar effect is observed in reactions of lithium 2-norbornyl-(alkyl)cuprates: only when alkyl = *tert*-butyl do these complexes transfer 2-norbornyl in conjugate additions to mesityl oxide.[14] It may be possible to convert other mercury(II) alkyls to reactive ate complexes using organolithium derivatives other than *tert*-butyl.[17]

(17) The relative reactivities of alkyl groups in mixed lithium dialkylcuprates, RR′CuLi, are difficult to predict; *cf.* W. H. Mandeville and G. M. Whitesides, *J. Org. Chem.*, **39**, 400 (1974).

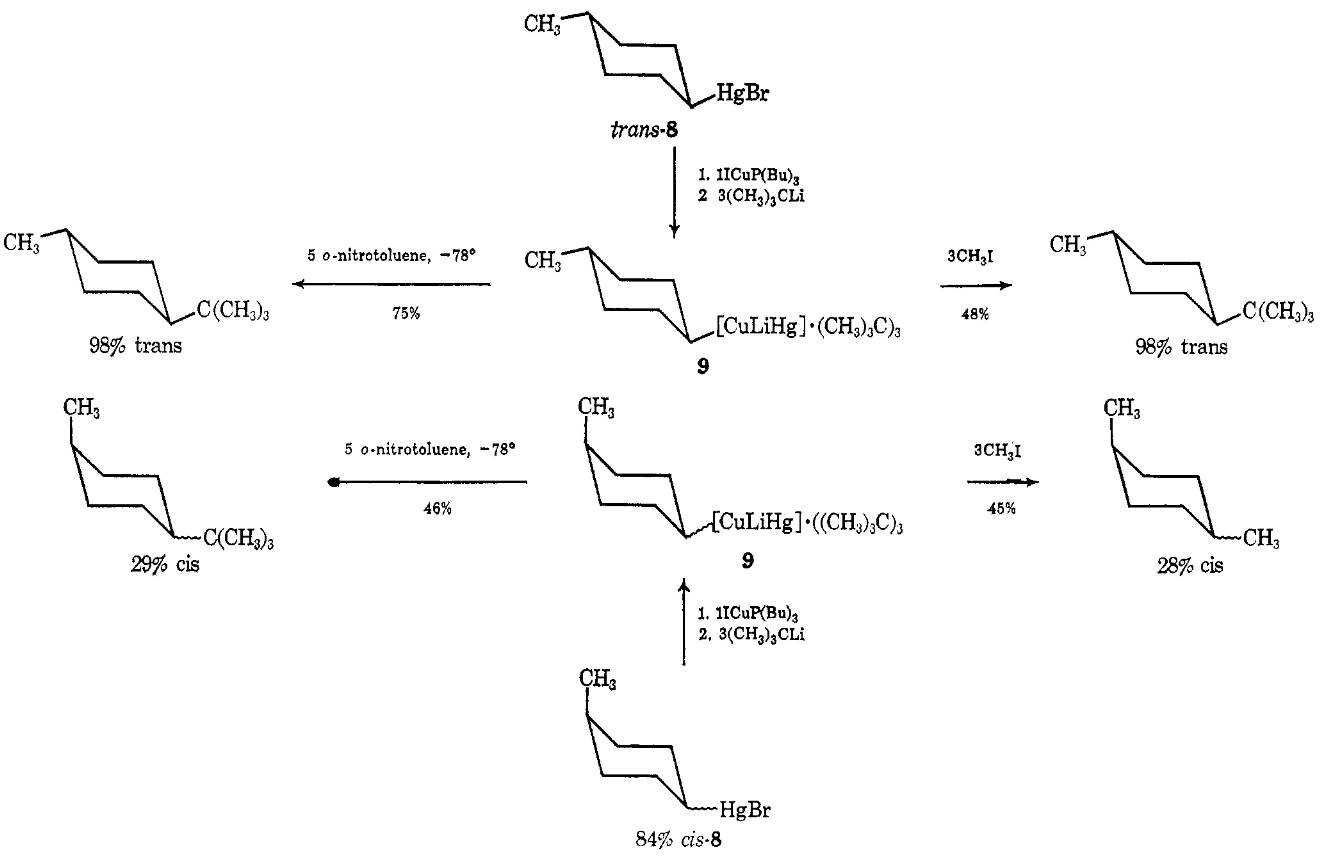
(18) F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *J. Amer. Chem. Soc.*, **82**, 2466 (1960).

(19) J. A. Landgrebe and R. D. Mathis, *J. Amer. Chem. Soc.*, **88**, 3545 (1966).

(20) E. LeGoff, S. E. Ulrich, and D. B. Denney, *J. Amer. Chem. Soc.*, **80**, 622 (1958).

(21) The extent of retention of configuration reported in Table I represents a minimum value. Jensen has stated[22] that his reported value of $[\alpha]^{25}D$ 25.8° [18] for D-(+)-*sec*-butylmercuric bromide probably is slightly low. Based on current estimates of the rotation of optically pure *sec*-butyl bromide[23] and the assumption that bromination of **5** in pyridine takes place stereospecifically with retention of configuration,[7,8] the rotation of optically pure **5** can be estimated to be in the range

Scheme II. Reactions of Ate Complexes Derived from *trans*-**8** Take Place with High Stereoselectivity; Products Derived from *cis*-**8** Are Extensively Epimerized



in stereochemistry apparently does not reflect racemization of the *sec*-butyl moieties of **6**, since the optical purity of **7** appears to be independent of the length of time that **6** is allowed to stand at −78° before alkylation with 1-iodohexane. Racemization might thus be occurring either during conversion of **5** to **6**, or during reaction of **6**.

In an effort to determine what variables lead to this lower stereoselectivity and also to examine another type of secondary alkylmercury reagent as starting material, we examined the ate complexes generated from *cis*- and *trans*-4-methylcyclohexylmercuric bromide (*cis*- and *trans*-**8**).[26] This substrate offers the experimental advantage over **5** that the diastereomeric composition of products derived from it can be assayed by glpc, without the exhaustive purification required for optical rotation measurements.

Experiments on samples highly enriched in either *cis*- or *trans*-**8** established that although high stereoselectivity is observed in reactions of the latter, products derived from the former are extensively epimerized (Scheme II). Indistinguishable stereochemical results were obtained when solutions of the reagents at room temperature were added to cold reaction mixtures and when the reagents were carefully precooled to −78° before mixing. The observation that the same stereoselectivity characterizes very different reactions—nucleophilic attack on methyl iodide and oxidative coupling induced by *o*-nitrotoluene—suggests that the epimerization that occurs during conversion of *cis*-**9** to products does not take place during reaction of the ate complex, but rather during its formation. A sample of **9** prepared from 96% *trans*-**8** yielded 98% *trans*-1,4-dimethylcyclohexane after standing for 2 hr at −78°; hence, as with **6**, there is no indication that the epimerization observed with **9** takes place after its formation. Thus, the majority of the epimerization of *cis*-**8**, and probably of **6**, must take place during the formation of these reagents. In fact, experiments outlined in Table II suggest that *cis*-**8** may react in a different manner than *trans*-**8**; specifically, transmetalation of either *cis*- or *trans*-**8** before addition of ICuP(Bu)$_3$ gives products with stereochemistry similar to those of *cis*-**8** in Scheme II. This observation suggests that in the case of *cis*-**8** free lithium reagent or some other organometallic species capable of epimerization exists during the formation of the complex **6**.

Other Potential Applications of Organomercury-Derived Ate Complexes. The stereochemical experiments already outlined indicate that the degree of success with which diastereomeric copper(I) ate complexes can be

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$[\alpha]^{25}\mathrm{D}$ 25.9–27.9° (*cf.* Experimental Section). The values in Table I were calculated on the assumption that the rotation of optically pure **5** is $[\alpha]^{25}\mathrm{D}$ +25.8° (*c* 4, EtOH), and that for optically pure **7** is $[\alpha]^{25}\mathrm{D}$ +9.3° (neat).[24] These calculations assumed that enantiomeric purity is linearly related to optical purity.[25]

(22) Reference 7, p 91.

(23) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969).

(24) R. L. Letsinger and J. G. Traynham, *J. Amer. Chem. Soc.*, **72**, 849 (1950). Other lower values for the specific rotation of 3-methylnonane have been reported.[20] However, the higher value of $[\alpha]^{25}\mathrm{D}$ 9.3° seems most accurate, since the synthesis giving this value did not involve any reaction at the asymmetric center.

(25) For one instance in which this assumption is invalid, *cf.* A. Horeau, *Tetrahedron Lett.*, 3121 (1969).

(26) F. R. Jensen and L. H. Gale, *J. Amer. Chem. Soc.*, **82**, 145 (1960).

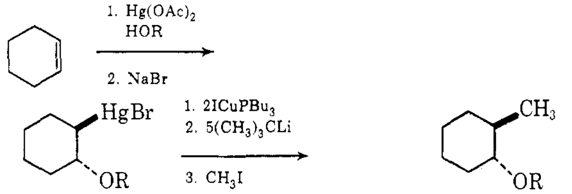
Table II. Reactions of Ate Complexes Prepared from 4-Methylcyclohexylmercuric Halides

	Products			
	from CH_3I		from $PhNO_2$	
Stereochemistry of **8** (% trans)	Yield, %	Stereochem (% trans)	Yield, %	Stereochem (% trans)
96	48	98	77	98
32	51	72	42	71
16	55	72	46	71
96[a]	55	70		
16[a]	58	70		

[a] *tert*-Butyllithium was added before $ICuPBu_3$ in this instance. In all others, $ICuPBu_3$ was added before *tert*-butyllithium.

generated from the analogous alkylmercury reagents depends upon the structure of the alkyl group involved in a way that is not presently entirely understood. In favorable cases, the generation and utilization of the functional equivalent of diastereomeric or enantiomeric carbanions may have practical application in synthetic or mechanistic studies, even if accompanied by a certain amount of epimerization. Regardless of stereochemical outcome, a method of increasing the reactivity of organomercury reagents by ate complex formation might be useful in synthesis.

We have examined briefly the behavior of representative organomercury reagents that can be obtained conveniently by procedures that do not require intermediate organomagnesium or -lithium reagents, *viz*., mercuration, oxymercuration[27] and mercury–boron interchange.[28] The formation and reaction of the ate complexes used in these experiments were carried out using procedures similar to those already described: a THF solution of the organomercuric halide was treated at −78° with 1 or more equiv of $ICuPBu_3$, and then with a several-fold excess of *tert*-butyllithium; the precise conditions chosen depended upon the presence or absence of other functional groups (*e.g*., OH) in the molecule that could consume organometallic reagents. The resulting solution of ate complex was allowed to stir for 15 min at −78°, and was treated with the indicated reagent. Conversion of *trans*-1-hydroxycyclohexyl-2-mercuric bromide into a reactive copper(I) ate complex and subsequent alkylation of this material take place in satisfactory yield. The overall transformation occurs with complete retention of configuration. Although the stereochemistry of this reaction should not be taken too seriously since the analogous cis diastereomer was not available for study, the procedure appears to offer a method of generating the functional equivalent of an α-hydroxy carbanion. Attempts to carry out a similar transformation starting with *trans*-1-methoxycyclohexyl-2-mercuric bromide failed, presumably because of elimination yielding cyclohexene. Other oxymercuration products will serve as substrates in this reaction, but the yield of alkylated product is quite sensitive to experimental conditions[29] and to the substrate used. For example, the ate complex from *erythro*- or *threo*-3-hydroxy-2-butylmercuric bromide gives no alkylated product on treatment with iodomethane, while that from 2-hydroxyoctylmercuric bromide yields 5-undecanol in 21% yield on treatment with iodopropane.



trans-**10**

R = H 41% yield, 98% + trans
R = CH_3, 0% yield

Arylmercurials do not react in the same manner as alkylmercurials. For example, the complex formed by phenylmercuric bromide, $ICuPBu_3$, and *tert*-butyllithium does form *tert*-butylbenzene if oxidized with nitrobenzene within 15 min after mixing the components. This complex does not react with alkyl halides to form alkyl benzenes. After 15 min at −78° the complex becomes quite unreactive, both chemically and thermally.

Primary organomercury compounds can be readily prepared from olefins *via* hydroboration–mercuration. These primary organomercury reagents react rapidly to form copper(I) ate complexes. The alkyl group originally bound to mercury is usually transferred in good yield (50–60% by glpc, 30–40% isolated) to an alkyl halide. The ate complex from ethyl 11-(bromomercuri)undecanoate did not, however, react with methyl iodide: the ethyl undecanoate recovered on work-up of the reaction mixture may result from enolization of the ester functionality.

Taken together, these experiments indicate that ate complex formation provides a possible method of increasing the reactivity of a number of unreactive organomercury compounds available by oxymercuration and hydroboration procedures, and thus renders these classes of materials useful as reagents in certain types of organic syntheses.

Conclusions

Reaction of alkylmercuric halides with *tert*-butyllithium in the presence of a soluble copper(I) halide generates an ate complex that appears to incorporate all three metallic elements. The reactivity of the alkyl group originally bonded to mercury may be significantly enhanced by this complex formation, to a level only slightly less than that characterizing lithium dialkylcuprates: these materials react with alkyl halides and with oxidizing agents; they do not react with α,β-unsaturated ketones under conditions we have examined. In certain instances (*e.g*., **1**, **5**, *trans*-**8**, *trans*-**10**), these reactions occur with useful stereoselectivity; in others, reaction results in epimerized product.

The nature of the factors responsible for the extensive epimerization observed on reactions of ate complexes derived from *cis*-**8**, the tolerable racemization

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(27) W. Kitching, *Organometal. Chem. Rev*., **3**, 35, 61 (1968); A. G. Makarova and A. N. Nesmeyanov, "Methods of Elemento-organic Chemistry," Vol. 4, North Holland Publishing Co., Amsterdam, 1967; L. G. Makarova in "Organometallic Reactions," Vol. 2, E. I. Becker and M. Tsutsui, Ed., Wiley, New York, N. Y., 1971, p 335 ff; Vol. 1, 1970, p 119 ff; T. G. Traylor, *Accounts Chem. Res*., **2**, 152 (1969); W. Kitching, *Rev. Pure Appl. Chem*., **19**, 1 (1969); H. C. Brown and P. J. Geoghegan, Jr., *J. Org. Chem*., **37**, 1937 (1972). Asymmetric oxymercuration has been discussed by J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice Hall, New York, N. Y., 1971, p 266 ff.

(28) R. C. Larock and H. C. Brown, *J. Organometal. Chem*., **26**, 35 (1971), and references therein.

(29) The presence of >2 equiv of lithium alkoxide in the presence of *trans*-**10** causes the ate complex formation to fail completely. This effect is presumably related to the decreased reactivity of "mixed" lithium diorganocuprates that contain alkoxy groups; *cf*. ref 17.

occuring with those obtained from **6**, and the essentially complete stereospecificity characterizing reaction of complexes obtained from **1** are not evident from the available data. The observation that the stereochemical outcome of these reactions is not a thermodynamic mixture and is independent of the time between the preparation and utilization of the reagents establishes that the ate complexes are configurationally stable. The observation that the same stereochemical outcome characterizes the two very different types of reactions studied most carefully during this work—nucleophilic and oxidative coupling—strongly suggests that the loss of stereochemistry observed in reaction of certain of the ate complexes is not related to the coupling reactions themselves. Thus, it appears that the loss in stereochemistry occurs during formation of the ate complexes. Metal–halogen exchange reactions are believed to involve free radicals, at least in part;[30] it seems possible, although unlikely, that radicals may be involved in these transmetalations. More believable is the possibility that certain of the organometallic species formed immediately on mixing the reagents are more prone to epimerization than are the ate complexes finally present when the system has reached equilibrium. This hypothesis is supported by the observation that mixing organolithium reagent with alkylmercuric halide in the absence of copper(I) salts followed by formation and reaction of a copper(I) ate complex results in extensive loss of stereochemistry in the products, even with **1**. Efforts to circumvent this problem by attempting to prepare the copper(I) ate complexes by reaction between organomercury compound and preformed cuprates have not led to significantly different stereochemical results. In the absence of detailed information concerning the composition of solutions containing "lithium dialkylcuprates" and organolithium–organocopper(I) ate complexes of other stoichiometries, this type of experiment neither proves nor disproves the original hypothesis. Regardless, this procedure holds promise as a method of preparing solutions that contain the functional equivalent of certain types of enantiomeric and diastereomeric carbanions, and provides a method of increasing the reactivity of many organomercury reagents to a level which makes them useful in organic synthetic procedures.

Experimental Section

General Methods. All reactions of air and water sensitive organometallics were carried out in flame-dried glassware under prepurified nitrogen using standard techniques.[31] Diethyl ether was distilled from calcium hydride under nitrogen; tetrahydrofuran and other ethereal and hydrocarbon solvents were distilled from a purple solution or suspension of disodium benzophenone dianion prior to use. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Nmr spectra were recorded on a Varian T-60 spectrometer. Infrared spectra were taken in sodium chloride cavity cells using a Perkin-Elmer Model 537 grating spectrometer. F&M Model 810 gas chromatographs were used for glpc analyses. Mass spectra were taken on a RMU-6E Hitachi Perkin-Elmer mass spectrometer. Lithium reagents were purchased from the Foote Mineral Co. as hydrocarbon solutions. Other reagents were purchased from commercial sources in reagent quality. Organolithium reagents were analyzed using the double titration method of Gilman.[32] Optical rotations were measured with a Perkin-Elmer Model 141 polarimeter in 1-dm cells. Tetrakis[iodo(tri-*n*-butylphosphine)-copper(I)] was prepared by a published procedure.[33] *exo*-Bicyclo[2.2.1]heptyl-2-mercuric bromide (*exo*-**1**) had mp 169.5–170.0° (lit.[9] mp 169.0–169.5°); *endo*-**1**[5] had mp 120–121° (lit.[9] mp 120.5–121.5°).

Resolution of (*S*)-(+)-*sec*-Butylmercuric Bromide (5). Using the procedure of Landgrebe and Mathis,[19] (+)-*sec*-butylmercuric bromide was resolved as the mandelic acid salt. In our hands, two or three recrystallizations of the (+)-*sec*-butylmercuric (+)-mandelate from absolute ethanol at 0° were sufficient to give (*S*)-(+)-*sec*-butylmercuric bromide of *ca.* 30% optical purity after work-up.[34,35]

***trans*-4-Methylcyclohexyl-1-mercuric bromide (*trans*-8),** obtained by the procedure of Jensen and Gale,[26] had mp 156.5–157.5° (lit.[26] mp 157.7–158°); ir (KBr pellet) 1449 (s), 1379 (s), 1302 (m), 1169 (s), 1060 (m), 1005 (m), 961 (m), 908 (m) cm^{-1}. The diastereomeric purity of this material was assayed by converting it to 4-methyl-1-bromocyclohexane,[36] followed by glpc analysis. In a typical experiment, *ca.* 0.4 g (*ca.* 1 mmol) of **8** was dissolved in 10 ml of pyridine. A solution of bromine (0.5 ml) in pyridine (10 ml) was added slowly to the solution containing **8** at 0° until the bromine no longer was decolorized. The resulting reaction mixture was poured into 100 ml of 5 *N* aqueous hydrochloric acid solution and extracted with three 25-ml portions of ether. The combined ethereal extracts were washed with two 50-ml portions of water to remove residual pyridine, and analyzed by glpc using a 8 ft × 0.125 in. 10%-Carbowax 20M on Chromosorb P column at 80°; *trans*-4-methyl-1-bromocyclohexane elutes before *cis*-4-methyl-1-bromocyclohexane on this column.

***cis*-4-Methylcyclohexylmercuric Bromide (*cis*-8).** A mixture composed of 84% *cis*-**8** and 16% *trans*-**8** was obtained by repeated fractional crystallization of an epimeric mixture of **8** composed of *ca.* 40% cis material, first from ethanol and then from pentane. Attempts to separate these diastereomers by chromatography under a variety of conditions were unsuccessful, and in fact appeared to result in epimerization of the material applied to the column.[10] The diastereomeric purity of **8** was assayed as described above. The material having 84% *cis*-**8** had mp 107–111° and a different infrared spectrum (KBr pellet): 1449 (s), 1441 (s), 1379 (m), 1371 (m), 1340 (s), 1303 (s), 1236 (s), 1169 (m), 1161 (s), 1100 (s), 1011 (m), 967 (m), 666 (s) cm^{-1}.

***trans*-2-Hydroxycyclohexylmercuric bromide (*trans*-9)**[9] had mp 150–152° dec (lit.[9] mp 150.5–151.5° dec).

***exo*- and *endo*-2-methylnorbornane (*exo*- and *endo*-3).** A mixture of 63 g (0.47 mol) of dicyclopentadiene and 60 g (1.42 mol) of propene was heated in a bomb for 2.5 hr at 230°.[37] The product mixture was distilled and 20 g of colorless liquid was obtained at 55° (88 Torr) (lit.[38] 115.5–115.8° (741 Torr)). To 3.33 g of 5-methyl-2-norbornene in 50 ml of ethyl acetate was added 0.30 g of platinum oxide. The mixture was hydrogenated under atmospheric pressure for 4 hr until the theoretical amount of hydrogen was absorbed. Removal of solvent and distillation yielded 2.98 g of colorless liquid at 50° (74 Torr) (lit.[38] 125.7–126.1° (747 Torr)). Vapor phase chromatography on a 0.25 in. × 18 ft SE-710 column at 90° yielded two peaks at 15.3 min (2-*exo*-methylnorbornane) and 16.3 min (2-*endo*-methylnorbornane) with relative areas of 1:3.4, respectively (lit.[38] 1:3.3). The infrared spectra of samples collected from this column were indistinguishable from those reported by Belikova and coworkers.[38,39]

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(31) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

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(33) G. B. Kaufman and L. A. Teter, *Inorg. Syn.*, **7**, 9 (1963).

(34) Use of 1:1 glyme–dioxane[19] for these recrystallizations occasionally led to decomposition of the mercurial. Decomposition during recrystallization from ethanol was less important.

(35) According to House and coworkers the specific rotation of (+)-2-bromobutane is between 33.4 and 35.7°. Since Jensen[7] states that (*S*)-(+)-*sec*-butylmercuric bromide ($[\alpha]^{25}\mathrm{D}$ 25.8° (*c* 4, EtOH)) gives (+)-2-bromobutane, $[\alpha]^{25}\mathrm{D}$ 33.1°, and that this bromination proceeds with complete retention, the actual value for (*S*)-(+)-*sec*-butylmercuric bromide must lie somewhere between 25.9 and 27.9°. All our values for stereoselectivities and optical purities in this paper are based on the lowest figure, *i.e.*, $[\alpha]^{25}\mathrm{D}$ 25.8° for the organomercurial, and therefore are minimum values.

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(39) Both *exo*- and *endo*-**3** were first prepared in these laboratories by Dr. A. Fang; *cf.* A. Fang, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1966.

exo-**2-*tert*-Butylbicyclo[2.2.1]heptane** (*exo*-**4**), prepared from norbornene and *tert*-butyllithium following a literature procedure,[40,41] had bp 55–57° (10 Torr) (lit.[40] bp 30° (0.4 Torr)); nmr ($\mathrm{CCl_4}$) δ 0.82 (s, *tert*-butyl), 1.0–2.9 (m), 2.2 (broad s).

endo-**2-*tert*-Butylnorbornane** (*endo*-**4**) was prepared by oxidative coupling of lithium *tert*-butyl(*endo*-2-norbornyl)cuprate at −78° with nitrobenzene.[42,43] The *endo*-**4** thus prepared could be distinguished from *exo*-**4** both by glpc retention times on a SE-30 or Carbowax 20M column and by nmr (the *tert*-butyl resonance comes at δ 0.82 for *exo*-**4** and δ 0.92 for *endo*-**4**).[41]

cis-**4-*tert*-Butylmethylcyclohexane.** Hydrogenation of 35.6 g (0.2 mol) of 4-*tert*-butylbenzoic acid in glacial acetic acid with 2.0 g of platinum oxide as catalyst and recrystallization as described by Stolow[44] yielded 10.0 g (28%) of *cis*-4-*tert*-butylcyclohexanecarboxylic acid, mp 117–118.5° (lit.[44] mp 117–118°). The carboxylic acid (13 g, 70 mmol) was then reduced with diborane in THF according to the procedure of Brown and Rao[45] to give 13.6 g (80%) of *cis*-4-*tert*-butylcyclohexylcarbinol as a waxy solid which could be distilled: bp 95° (1.3 Torr) (lit.[46] bp 133–136° (27 Torr)); ir ($\mathrm{CCl_4}$) 3610 (w), 3300 (b), 2940 (s), 1470 (s), 1445 (s), 1360 (s), 1025 (s) cm^{-1}; nmr ($\mathrm{CCl_4}$) δ 3.5 (d), 3.3 (s, OH), 2.0–1.0 (m), 0.9 (s, $\mathrm{C(CH_3)_3}$). This alcohol (6.3 g, 37 mmol) was allowed to react with 60 ml of a pyridine solution containing 15.7 g (87 mmol) of *p*-toluenesulfonyl chloride according to the procedure of Mori[46] and yielded 10.4 g (87%) of *cis*-4-*tert*-butylcyclohexylmethyl tosylate: mp 93–94° (lit.[46] mp 95–95.5°); nmr ($\mathrm{CCl_4}$) δ 7.5 (4 H, m), 3.0 (2 H, d), 2.4 (3 H, s), 1.8–1.0 (10 H, m), 0.8 (9 H, s). The tosylate was reduced with lithium aluminum hydride in an adaptation of the procedure used by Wiberg and Pfeiffer.[47] A mixture of 6.5 g (20 mmol) of the tosylate and 0.84 g (22 mmol) of lithium aluminum hydride in 60 ml of ether was refluxed for 2 days. The reduction was worked up as described by Fieser and Fieser[48] to give 1.5 g (50%) of crude product which was distilled, bp 84° (22 Torr) (lit.[49] bp 188.8°). The product *cis*-4-*tert*-butyl-1-methylcyclohexane was further purified by preparative glpc and had nmr ($\mathrm{CCl_4}$) δ 2.0–1.2 (m), 0.92 ($\mathrm{—CH_3}$, d), 0.9 ($\mathrm{—C(CH_3)_3}$, s).

trans-**4-*tert*-Butyl-1-methylcyclohexane.** Using a published procedure,[50] 3.2 g (32%) of *trans*-4-*tert*-butylcyclohexanecarboxylic acid, mp 175.5–176.5 (lit.[50] mp 176–177°), was prepared from 10 g of crude 4-*tert*-butylcyclohexanecarboxylic acid. Using procedures described above, the acid was reduced to 4.2 g (91%) of crude *trans*-4-*tert*-butylcyclohexylmethanol. This crude product was not distilled but was treated with 9.5 (50 mmol) of *p*-toluenesulfonyl chloride in 50 ml of pyridine as described by Mori[46] to give 6.9 g (86%) of *trans*-4-*tert*-butylcyclohexylmethyl tosylate, mp 82.5–83.5° (lit.[46] mp 83–84°). Using the procedures described above for the cis isomer, 6.5 g (20 mmol) of this tosylate was reduced with 1.0 g (*ca.* 25 mmol) of lithium aluminum hydride. The product *trans*-4-methyl-*tert*-butylcyclohexane[49] was purified by glpc on a 0.25 in. × 8 ft SE-30 column and had nmr ($\mathrm{CCl_4}$) δ 2.0–1.4 (m), 0.85 ($\mathrm{CH_3}$, d), 0.83 ($\mathrm{C(CH_3)_3}$, s); ir ($\mathrm{CCl_4}$) 1475 (s), 1465 (s), 1445 (s), 1390 (m), 1363 (s), 1243 (s) cm^{-1}. The trans isomer was distinguished from the cis isomer in the nmr by the chemical shift of the methyl doublet at 0.85 and 0.92 ppm, respectively. The ir ($\mathrm{CCl_4}$) spectra of both isomers were virtually identical with the exception that the cis isomer has a strong peak at 1243 cm^{-1}, whereas the trans isomer has a strong peak at 1233 cm^{-1}. Glpc analysis used a 0.125 in. × 8 ft SE-30 on Chromosorb W column, the trans isomer eluting first.

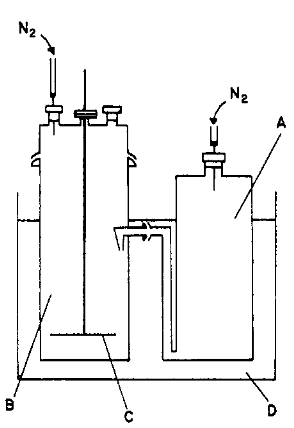

Figure 1. Apparatus for low-temperature, slow addition of reagent: (A) precooled reagent flask; (B) reaction vessel; (C) Vibromixer; (D) cooling bath.

General Procedures for the Preparation and Utilization of Ate Complexes from Alkylmercury Compounds, Tetrakis[halo(tri-*n*-butylphosphine)copper(I)], and *tert*-Butyllithium. The alkylmercury compound (1 mmol) was placed in a dry, 40-ml centrifuge tube containing a magnetic stirring bar and an appropriate amount of an internal glpc standard, and the tube was stoppered and flushed with nitrogen. THF (20 ml) was added, and the resulting solution cooled to −78°.[51] A −78° THF solution (10 ml) containing $\mathrm{[ICuP(\mathit{n}\text{-}Bu)_3]_4}$ (0.393 g, 0.25 mmol of the tetramer, 1 mequiv) was added, and the resulting solution was stirred for 5 min at −78°. Slow addition of 3 mmol of *tert*-butyllithium (*ca.* 3 ml of a 1.0 *N* solution in pentane) yielded a yellow solution of the ate complex. This solution was allowed to stir for *ca.* 5 min, and then used; permitting the solution to stir for longer times had no discernible influence on the yield or stereoselectivity of these ate complexes. The addition of the *tert*-butyllithium to the solution containing RHgX and $\mathrm{ICuPBu_3}$ was significantly exothermic. To minimize the influence of local heating on the stereochemistry of the copper ate complex, the *tert*-butyllithium solution in a separate, stoppered, centrifuge tube was cooled to the temperature of the solution to which it was to be added, and then added very slowly, with vigorous stirring, through a stainless steel cannula. This precaution was particularly necessary when larger quantities of reagents were utilized in preparative scale reactions involving diastereomeric or enantiomeric organomercury reagents.

Alkylation of the ate complex prepared using this procedure was accomplished by adding 3 mmol of alkylating agent dropwise by syringe either neat or in THF or pentane.[23] The resulting solution was allowed to stir at −78° for 30 min, then hydrolyzed by addition of 0.1 ml of concentrated HCl at −78° or by pouring into saturated aqueous ammonium chloride solution. The hydrocarbon phase of the resulting solution was analyzed directly by glpc.

Oxidative coupling of the alkyl groups present in these ate complexes was carried out by adding an excess (*ca.* 1 ml) of nitrobenzene to the solution of ate complex at −78°.[21,52] The resulting deep red solution was allowed to stir at −78° for 30 min, hydrolyzed by addition of 0.1 ml of concentrated HCl, and analyzed by glpc.

Preparation of (+)-3-Methylnonane from D-(+)-*sec*-Butylmercuric Bromide. Using the procedure described involving precooled reagents and the apparatus shown in Figure 1, 10.1 g (30 mmol) of D-(+)-*sec*-butylmercuric bromide, $[\alpha]^{25}\mathrm{D}$ 8.5° (*c* 3, EtOH), was dissolved in 50 ml of THF and a cooled solution of 11.8 g (7.5 mmol) of $\mathrm{[ICuPBu_3]_4}$ in 50 ml of THF or 4:1:1 THF–ether–pentane[51] was added from the addition flask. This solution was converted into an ate complex on addition of 90 ml of a 1 *N* pentane solution of *tert*-butyllithium (90 mmol) over 1.0 hr at −78 or −117°. This apparatus was designed to permit slow addition of the cold (temperatures as low as −117°) solution of organolithium reagent with vigorous stirring and without the inconvenience and

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[51] When reactions were carried out at −117° (pentane–liquid nitrogen slush), a solvent system with a lower freezing point was used—4:1:1 THF–ether–pentane: *cf.* G. Köbrich and H. Trapp, *Chem. Ber.*, **99**, 670 (1966).

[52] If nitrobenzene or its reaction products interferred with glpc analysis or isolation, another nitroaromatic compound was used. The yield in these coupling reactions is not very sensitive to the nature of the oxidant.

leakage of air into the reaction mixture that commonly occurs with high-speed stirring. After formation of the ate complex, 1-iodohexane (15 ml, 100 mmol) dissolved in 15 ml of pentane was added slowly from the reagent part of the apparatus. The reaction mixture was allowed to stir for 15 min, then hydrolyzed by addition of 100 ml of a mixture of 10 ml of concentrated HCl in 90 ml of methanol. The hydrolyzed reaction mixture was poured into 200 ml of H_2O and allowed to come to room temperature. The ether layer was separated and the aqueous layer extracted with two 100-ml portions of pentane. The combined organic phase was dried ($MgSO_4$) and concentrated to *ca.* 50 ml using a rotary evaporator at room temperature. The resulting crude product was dissolved in 50 ml of pyridine and treated with a solution of 5 g of bromine in 20 ml of pyridine until the bromine color persisted. The bromination reaction mixture was then cautiously poured into 100 ml of 1 *N* HCl. The organic layer was separated and the aqueous phase was washed with two 50-ml portions of pentane. The combined organic phase was washed with four 100-ml portions of 1 *N* HCl to remove residual pyridine. The pentane solution was concentrated to a volume of *ca.* 25 ml, applied to the top of a 2 × 15 cm column containing *ca.* 40 g of Woelm activity I alumina, and eluted using pentane. Slightly over one column volume (60 ml) of pentane was collected. Vpc analysis of the solution showed 2,2-dimethyloctane, 3-methylnonane, and traces (<5%) of 1-iodohexane. This solution was concentrated to a volume of *ca.* 2 ml, and the 3-methylnonane was purified by preparative glpc using a 0.25 in. × 8 ft, SE-30 on Chromosorb W column; $[\alpha]^{25}\text{D}$ typically $+2.0°$ (*c* 5, pentane) (lit.[24] $[\alpha]^{25}\text{D}$ $+9.3°$ (neat)).

***trans*-2-Methylcyclohexanol by Methylation of the Ate Complex Formed from 2-Hydroxycyclohexylmercuric Bromide, Copper(I), and *tert*-Butyllithium.** Starting with *trans*-2-hydroxycyclohexylmercuric bromide, the ate complex was prepared by the procedure described involving precooled reagents, with the modification that 2 mequiv of $ICuP(n\text{-Bu})_3$ and 5 mmol of *tert*-butyllithium was used because of the presence of the hydroxyl proton in the mercurial. Reaction with methyl iodide (2.1 g, 15 mmol) for 1 hr at −78° followed by stirring for 1 hr at 0° and hydrolysis with 1 ml of concentrated hydrochloric acid gave a 41% yield of 2-methylcyclohexanol (98% trans, 2% cis). The yield and stereochemical purity were determined by analysis by glpc using a 0.125 in. × 8 ft TCEP on Chromosorb P column.

Ethyl 11-bromomercuriundecanoate was prepared in 85% yield following the procedure of Larock and Brown[53] and had mp 80–81°; ir (Nujol mull) 1737, 1311, 1278, 1241, 1206, 1179, 1089, 772, 720, and 680 cm⁻¹.

Anal. Calcd for $C_{13}H_{25}BrHgO_2$: C, 31.61; H, 5.10. Found: C, 31.46; H, 5.15.

Octadecylmercuric bromide was prepared from the Grignard reagent as described by Meals and had mp 110.5–111.5° (lit.[54] mp 110–111°); ir (Nujol mull) 1456 (s), 1375 (s), 707 (s), and 679 (s) cm⁻¹.

***threo*-3-Bromomercuributan-2-ol** was prepared from *cis*-2-butene and mercuric acetate using the procedure of Hofmann and Sands.[55] The mercurial was recrystallized from ethyl acetate at −20° and had mp 65–66° dec; ir (KBr pellet) 3415 (broad), 2980 (s), 2955 (s), 2930 (s), 1448 (s), 1375 (s), 1161 (s), 1140 (m), 1098 (s), 1068 (s), 1003 (s), 962 (m), 910 (s), 886 (m) cm⁻¹; nmr ($CDCl_3$) δ 4.30 (m), 3.00 (m), 1.90 (broad s), 1.43 (d), 1.33 (d).

Anal. Calcd for C_4H_9BrOHg: C, 13.59; H, 2.56. Found: C, 13.58; H, 2.67.

***erythro*-3-Bromomercuributan-2-ol** was prepared from *trans*-2-butene and mercuric acetate using the procedure of Hofmann and Sands.[55] The mercurial was recrystallized from ethyl acetate at −20° and had mp 80.5–81.5° dec; ir (KBr pellet) 3300 (broad s), 2980 (s), 2955 (s), 2930 (s), 1442 (s), 1378 (s), 1367 (s), 1305 (s), 1285 (m), 1175 (s), 1101 (s), 1095 (s), 1060 (s), 1021 (m), 1005 (s), 912 (s), 890 (s) cm⁻¹; nmr ($CDCl_3$) δ 4.34 (m), 3.07 (m), 2.07 (broad s), 1.43 (d), 1.33 (d).

Although these two diastereomers have similar spectra, it was possible to determine the diastereomeric composition of their mixtures with $Eu(fod)_3$ as a shift reagent. In the shifted spectra, the methyl groups α to the hydroxyl could be easily distinguished since they were separated by over 0.5 ppm.

Acknowledgments. We are indebted to our colleagues Dr. P. E. Kendall for authentic samples of conjugate addition products from norbornyl cuprates and mesityl oxide, to Mr. Craig Hill for a sample of *trans*-2-methoxycyclohexylmercuric bromide, and to Mr. Larry Trzupek for mass spectra.

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