Stereoselective Synthesis of 1-Substituted Organometallic Derivatives of 3,3-Dimethylbutane-$1,2$-d_2[1]

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Abstract: Reactions of *threo*-3,3-dimethylbutyl-$1,2$-d_2 brosylate (**2**) and triflate (**4**) with nucleophilic metal-containing species have been used to prepare *erythro*-3,3-dimethylbutyl-$1,2$-d_2 phenyl selenide (**3**), -pyridinecobaloxime (**5**), and -cyclopentadienyltricarbonylmolybdenum (**6**); each reaction takes place with inversion of configuration at carbon. Reaction of 3,3-dimethylbutyl-$1,2$-d_2 bromide (predominantly erythro) (**7**) with trimethyltin lithium yields trimethyl(3,3-dimethylbutyl-$1,2$-d_2)tin (**8**) with *ca.* 80% inversion of configuration. Treatment of cyclopentadienyldicarbonyliron *threo*-3,3-dimethylbutyl-$1,2$-d_2 (**1**) with mercuric chloride leads to *threo*-3,3-dimethylbutyl-$1,2$-d_2-mercuric chloride (**9**).

The usefulness of pure threo and erythro diastereomers having the composition $(CH_3)_3CCHDCHDX$ in the study of the stereochemical characteristics of reactions of transition metal alkyls has been illustrated in the preceding paper for X = Fe(CO)$_2$Cp (**1**).[3–6] The preparation of this substance involved nucleophilic displacement of brosylate ion from 3,3-dimethylbutyl-$1,2$-d_2 brosylate (**2**) by cyclopentadienyldicarbonyliron anion. In this instance, displacement proceeded relatively rapidly and in high yield. Despite the facility of this particular reaction, two characteristics of these reaction partners suggested that it might prove difficult to prepare other organometallic derivatives of the 3,3-dimethylbutyl skeleton without modification of this procedure. First, the cyclopentadienyldicarbonyliron anion is one of the strongest nucleophiles known;[7] second, SN2 substitution at C-1 of the 3,3-dimethylbutyl moiety is relatively hindered.[12] The low nucleophilicity of many of the metallate anions whose alkyl

derivatives are of potential mechanistic interest and the low reactivity of the 3,3-dimethylbutyl group are expected to combine to make the preparation of the alkylmetal species prohibitively slow under the conditions used in the preparation of **1**. The thermal lability of most transition metal alkyls is such that it is not practical to increase reaction rates by increasing reaction temperatures. Hence, one would not expect to be able to prepare organometallic derivatives of the 3,3-dimethylbutyl moiety by the alkylation of weakly nucleophilic metallate anions with **2**.

The work reported in this paper was carried out to provide procedures that could be used to obtain alkyl derivatives of a number of metals. Although little or no chemistry has been carried out on the organometallic compounds prepared during these studies, the range of metallic moieties that can be attached stereospecifically to the $(CH_3)_3CCHDCHD$ moiety establishes that a wide variety of organometallic substances containing this group can be prepared and indicates that this group of compounds should have general utility in the study of organometallic reaction mechanisms.

Results and Discussion

Reactions of **2** with cyclopentadienyldicarbonyliron anion and sodium phenyl selenide[13] yield the corresponding organometallic compounds **1** and **3** in good yields (Scheme I, Figure 1); in each case, carbon–metal bond formation occurs with greater than 95% inversion of configuration at carbon (Figure 1). Presumably, other comparably strong nucleophiles would react with **2** under similar conditions. In an effort to extend the range of metallate anions that can be alkylated by derivatives of 3,3-dimethylbutanol to include weakly nucleophilic species, we have examined the reactivity of 3,3-dimethylbutyl-$1,2$-d_2 trifluoromethylsulfonate (**4**) toward metallic anions. Not only does **4** react smoothly with the strong nucleophile[13,14] Co(dmgH)$_2$py$^-$ to yield the corresponding alkylcobaloxime, **5**, with >95% inversion of configuration at carbon,[15] but it also reacts

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(3) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. Demers, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **96**, 2814 (1974).

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(5) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **91**, 4313 (1969).

(6) See also H. L. Fritz, J. H. Espenson, D. A. Williams, and G. Q. Molander, *J. Amer. Chem. Soc.*, **96**, 2378 (1974).

(7) A comprehensive and consistent scale of nucleophilicities of important organic and organometallic nucleophiles is not available. Estimates of nucleophilicities toward methyl iodide obtained from a number of sources[8–11] leads to the following approximate values for n_{CH_3I}: Ph$_2$Bi$^-$ (14.3); Co(dmgH)$_2$py$^-$ (13.3); Ph$_3$Sn$^-$ (11.5); CpFe(CO)$_2^-$ (11.3); PhSe$^-$ (10.2); CN$^-$ (7.4); I$^-$ (7.3); OH$^-$ (6.5); N$_3^-$ (6.3); NH$_3$ (5.5); (CO)$_5$Mn$^-$ (5.4); CpMo(CO)$_3^-$ (5.3); (CO)$_4$Co$^-$ (3.5); CH$_3$OH (0.00). Since these data were obtained under a variety of reaction conditions, and using several different alkyl halides as substrates, they should not be taken as more than suggestive. They nonetheless emphasize the very high nucleophilicity of certain organometallic species toward carbon and indicate the broad range of nucleophilicities characterizing metallate anions.

(8) R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, **88**, 5121 (1966).

(9) G. N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.*, **91**, 3341 (1969); G. N. Schrauzer, E. Deutsch, and R. J. Windgassen, *ibid.*, **90**, 2441 (1968).
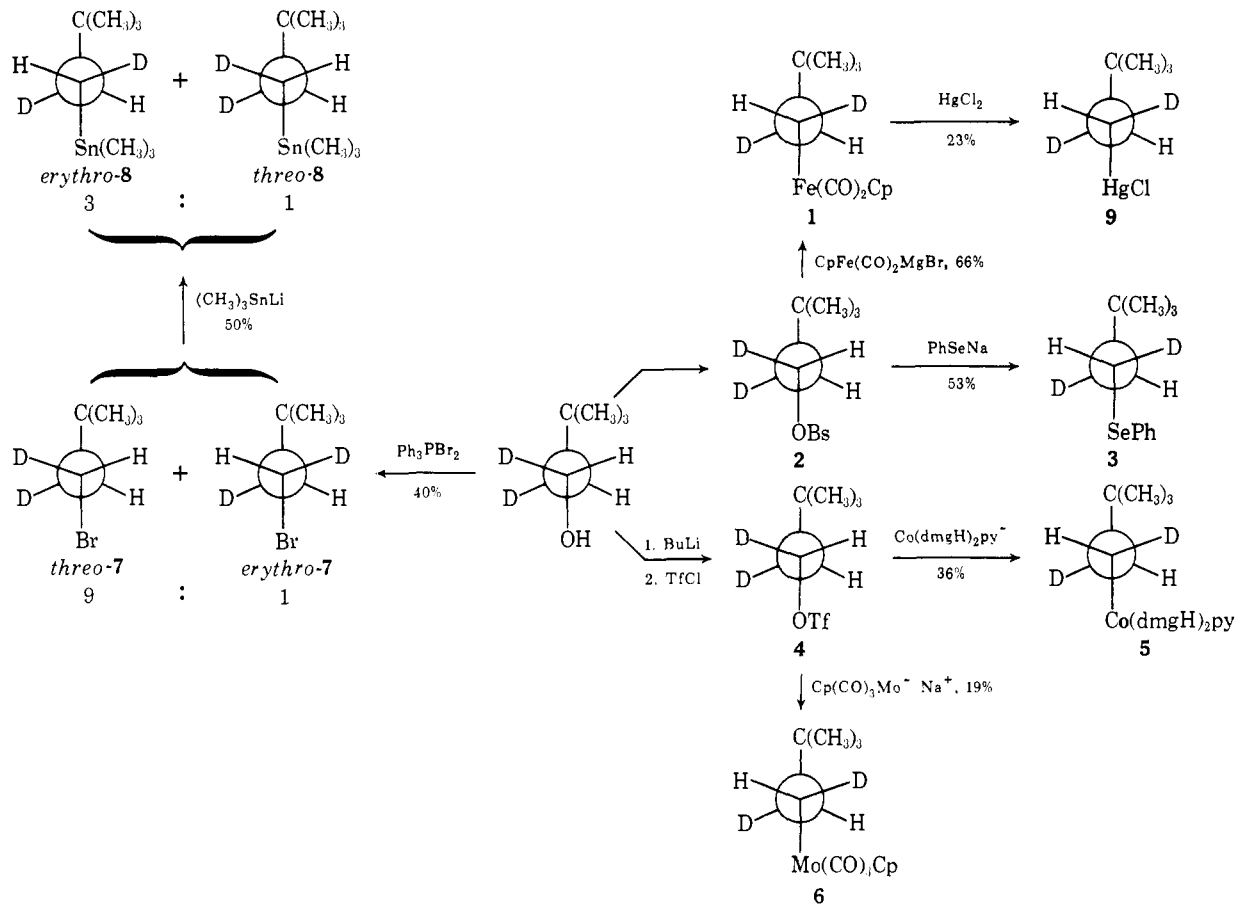
(10) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(11) R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968).

(12) The relative rates of reaction of neopentyl bromide, 3,3-dimethylbutyl bromide, and *n*-butyl bromide with potassium iodide in acetone are 0.0064:4.15:100: E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 79.

(13) Alkyl phenyl selenides have recently been shown to be reagents of significant synthetic utility: *cf.* K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, **94**, 7154 (1972); K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **37**, 3973 (1972); K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Lett.*, 2917 (1973); K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, **95**, 2697 (1973).

(14) D. Dodd and M. D. Johnson, *Organometal. Chem. Rev.*, **52**, 1 (1973).

Scheme I. Synthesis of Organometallic Derivatives of the 3,3-Dimethylbutyl-*1,2-d₂* Moiety

erythro-8   threo-8
3   :   1

(CH₃)₃SnLi
50%

threo-7   erythro-7
9   :   1

Ph₃PBr₂
40%

1. BuLi
2. TfCl

HgCl₂
23%

9

CpFe(CO)₂MgBr, 66%

1

PhSeNa
53%

2

3

Co(dmgH)₂py⁻
36%

4

5

Cp(CO)₃Mo⁻ Na⁺, 19%

6

rapidly with the relatively weakly nucleophilic[7] cyclo-pentadienyltricarbonylmolybdenum anion to yield **6**, again with inversion of configuration at carbon (Scheme I). The ability of **4** to alkylate the CpMo(CO)₃⁻ anion suggests that it should be possible to prepare 3,3-dimethylbutyl derivatives of a variety of chemically interesting but weakly nucleophilic metallate anions.[16]

Each of the displacement reactions leading to compounds **1, 3, 5,** and **6** takes place with clean inversion of stereochemistry at carbon. The single exception we have encountered to this stereochemical course for nucleophilic displacement by a metallate anion at C-1 of the 3,3-dimethylbutyl group occurred during reaction of trimethyltin lithium[17] with 3,3-dimethylbutyl-*1,2-d₂* bromide (**6**). This reaction was examined both because the trimethyltin anion is a strong nucleophile and because recent work has suggested that the reaction of trimethyltin lithium with certain secondary bromides proceeds with predominant *retention* of configuration at carbon.[18] Interpretation of this experiment is less

(15) Compound **2** has recently been converted to **5** by reaction with Co(dmgH)₂⁻ and **5** converted to *threo*-**9** with inversion of configuration by reaction with mercuric perchlorate.[6]

(16) Brosylate is among the most reactive of the commonly used leaving groups; triflates are approximately 10⁴⁻⁵ times as reactive as tosylates (and therefore about 10⁴ times as reactive as brosylates) in Sₙ2 reactions: R. L. Hansen, *J. Org. Chem.*, **30**, 4322 (1965); A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *J. Amer. Chem. Soc.*, **90**, 1598 (1968); T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **91**, 5386 (1969).

(17) C. Tamborski, F. E. Ford, and E. J. Soloski, *J. Org. Chem.*, **28**, 237 (1963).

(18) 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) The reaction of (CH₃)₃SnLi with secondary tosylates was shown to go with the expected inversion of configuration.
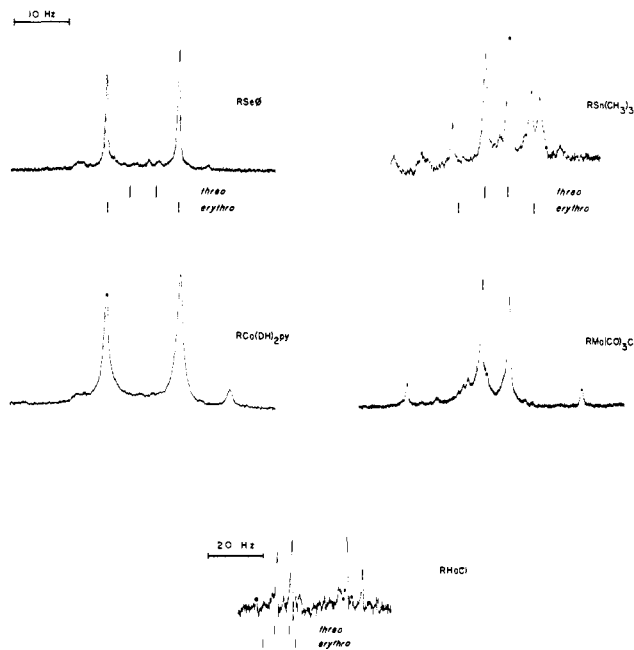
Figure 1. The deuterium-decoupled 100-MHz nmr spectra of the CHDM resonance of **3, 5, 8,** and **9,** and the CHDCHD resonances of **6.** Note that the spectrum of **9** shown is for threo material, although Scheme I indicates a transformation leading to erythro (see the text for an explanation).

clear-cut than that of others carried out during this work, because the starting bromide was itself a diastereo-

The interpretation of these experiments is clouded by the fact that only one diasteriomer of the possible pair of diasteriomeric alkyl bromides was examined in each instance.

meric mixture of 90% erythro and 10% threo diastereomers.[19] The deuterium-decoupled nmr spectrum of the trimethyl(3,3-dimethylbutyl-*1,2-d₂*)tin showed two overlapping AX patterns with $J = 4.2$ Hz and $J' = 14.2$ Hz in the ratio 3:1 (Figure 1). Hence, it appears that this alkylation reaction takes place with approximately 80% inversion of configuration at carbon. The relatively low diasteriomeric purity of the starting 7 and the absence of controls establishing that 8 is configurationally stable under the reaction conditions combine to suggest that the per cent inversion of configuration observed in this experiment should be taken as a minimum value. The predominant inversion of stereochemistry observed here differs from the predominant retention observed in reaction of trimethyltin lithium with several other alkyl bromides.[18] However, the 3,3-dimethylbutyl moiety differs substantially in structure from the organic groups examined previously, and the difference in the stereochemical outcome of these experiments may again only emphasize the sensitivity of the mechanism of these and other organometallic reactions to the structure of the organic groups involved.

It is also possible to synthesize organometallic compounds containing one diasteriomer of the 3,3-dimethylbutyl-*1,2-d₂* group by transmetallation. Thus, reaction of 1 with a suspension of mercuric chloride in benzene resulted in a useful yield of 3,3-dimethylbutyl-*1,2-d₂*-mercuric chloride (9);[20] this reaction takes place with greater than 90% retention of configuration.[21] Although we have not explored reactions of 1 (or others of the organometallic species prepared during this work) with other electrophilic metal species, the high reactivity of 1 toward other electrophiles[3] suggests that such reactions might be successful.

Experimental Section

General Methods. All reactions involving organometallics were carried out under nitrogen atmospheres. Prepurified nitrogen was dried by passage through a 12-in. tube containing Drierite. All solvents were reagent grade material. THF was distilled from a dark purple solution of benzophenone dianion before use. Ethanol and methanol were degassed by bubbling a vigorous stream of nitrogen through them.

All boiling points are uncorrected. Infrared spectra were taken in sodium chloride cells on a Perkin-Elmer Model 237 grating spectrophotometer. Routine nmr spectra were recorded on a Varian T-60 spectrometer; chemical shifts are reported in parts per million downfield from tetramethylsilane. Microanalyses were performed by Midwest Microlabs, Ltd., Indianapolis, Ind. Liquid samples for elemental and spectral analysis were purified by use of a Hewlett-Packard Model 700 thermal conductivity glpc. Deuterium-decoupled nmr spectra were obtained as described previously.[3]

Alkylation of Sodium Phenyl Selenide. Sodium phenyl selenide was prepared from diphenyl diselenide following a literature procedure.[22,23] A 50-ml, three-necked flask was equipped with a

magnetic stirring bar and nitrogen inlet and was charged with 0.62 g (2.0 mmol) of diphenyl diselenide and 25 ml of degassed anhydrous ethanol. The suspension was stirred, and sodium borohydride (0.15 g, 4.2 mmol) was added in portions until the solution changed from yellow to clear. An ethereal solution of the brosylate 2 (prepared as described previously from 4.0 mmol of *threo*-3,3-dimethylbutan-1-ol-*1,2-d₂*) was added in one portion, and the mixture was allowed to stir for 5 hr. The white salts were removed by centrifugation and washed with 10 ml of anhydrous ether, and the combined solution and washings were distilled through a 10-cm Vigreux distillation column, removing all material boiling below 100°. Light yellow crude product 3 (0.92 g, 2.2 mmol, 53%) remained. A sample of this material was purified by glpc using an 8-ft UCW-98 column held at 200° and had: ir (CCl₄) 3070, 2950, 2865, 1475, 1465, 1385, 1360, 1240, 1185, 1033, 855, 705 cm⁻¹; deuterium-decoupled nmr (CDCl₃) δ 0.88 (s, 9), 1.58 (d, 1, $J = 12.8$ Hz), 2.83 (d, 1, $J = 12.8$ Hz), 7.1–7.4 (m, 5).

A sample of d_0 material prepared in an analogous manner had the following elemental analysis.

Anal. Calcd for C₁₁H₁₅Se: C, 59.74; H, 7.51. Found: C, 60.01; H, 7.52.

Alkylation of Co(DH)₂pyNa. Cobaloxime anion was prepared on a 100-mmol scale using a literature procedure.[24] A 40-ml flame-dried centrifuge tube equipped with a No-Air stopper, nitrogen inlet, and a magnetic stirring bar was charged with 20 ml of degassed anhydrous ether and 0.52 g (5.0 mmol) of *erythro*-3,3-dimethylbutan-1-ol-*1,2-d₂*. A solution of 2.0 N *n*-butyllithium (2.5 ml, 5.0 mmol) was added by syringe to the cooled (ice), rapidly stirred solution. The solution turned cloudly and was allowed to stir at 0° for 5 min. Trifluoromethylsulfonyl chloride (0.85 g, 5.0 mmol) was added by syringe to the reaction mixture. The reaction mixture was allowed to warm to room temperature and was centrifuged. The supernatant liquid was transferred by forced siphon through a stainless steel cannula to a flask containing 2.5 mmol of a cold (−10°) solution of cobaloxime anion. The solution was allowed to stir and warm to room temperature, and then was poured into 25 ml of water. The resulting orange-brown crystals were collected by filtration, washed repeatedly with water, recrystallized by dissoving in methanol at room temperature, adding water, and chilling to −20°. The resulting orange-yellow crystals (413 mg, 0.90 mmol, 36%) had: ir (CHCl₃) 3360, 2950, 2860, 2460, 1600, 1550, 1450, 1360, 1200, 1085, 970 cm⁻¹; deuterium-decoupled nmr (CDCl₃) δ 0.76 (s, 9) 0.78 (obscured), 1.62 (d, 1, $J = 13.1$ Hz), 7.1–8.6 (m, 5). A sample of d_0 material prepared in an analogous manner had the following elemental analysis.

Anal. Calcd for C₁₉H₃₂N₅O₄Co: C, 50.34; H, 7.11; N, 15.44. Found: C, 50.60; H, 7.13; N, 15.74.

Alkylation of π-Cyclopentadienyltricarbonylmolybdenum Anion. A 25-ml flask was flame dried and equipped with a magnetic stirring bar, No-Air stopper, and nitrogen inlet. The flask was charged with 2 ml of mercury, rapid stirring was initiated, and 0.10 g (4.3 mg-atom) of sodium was added. After an induction period of several seconds, the sodium reacted suddenly and exothermically with the mercury to form an amalgam. Dried, degassed THF (25 ml) was added, followed by 0.98 g (2.0 mmol) of π-cyclopentadienyltricarbonylmolybdenum dimer, and the reaction was allowed to stir at room temperature for 3 hr. The cloudly reaction mixture was transferred by forced siphon through a stainless steel cannula into a flame-dried 40-ml centrifuge tube equipped with a No-Air stopper. After centrifugation the light yellow supernatant liquid was added dropwise by cannula to a cold (0°) ether solution of the triflate 4 (prepared as described above from 4.0 mmol of alcohol and 4.0 mmol of trifluoromethylsulfonyl chloride). An immediate color change from yellow to orange-red occurred. The reaction mixture was allowed to warm to room temperature and stir for 1 hr. The solvent was removed at 0.01 Torr and 25°, and the residue was extracted with pentane and chromatographed once on a 2 × 20-cm column of neutral Merck alumina and once on a 2 × 20-cm column of Merck acid-washed alumina (the material decomposes rapidly on neutral alumina, slowly on acid-washed material), using pentane as eluent. Removal of the pentane yielded 263 mg (0.77 mmol, 19%) of 6 as a yellow solid, mp 80–82°: ir (CCl₄) 2950, 2860, 2015, 1930, 1460, 1420, 1360, 1230, 910 cm⁻¹; deuterium-decoupled nmr δ 5.22 (s, 1), 1.56 (d, 1, $J = 13.3$ Hz), 1.44 (d, 1, $J = 13.3$ Hz), 0.87 (s, 9). The thermal stability of this material was too low to permit its combustion analysis.

Alkylation of Trimethyltin Lithium. Trimethyltin lithium was

(19) The preparation of 7 in high diasteriomeric purity has proved difficult on a synthetically useful scale, although the preparation of small quantities for nmr examination presents no difficulty.[3]

(20) A. N. Nesmeyanov, Y. A. Chapovsky, I. V. Polovyanyuk, and L. G. Makarova, *J. Organometal. Chem.*, 7, 329 (1967).

(21) This experiment has actually been carried out in the opposite enantiomeric series and is included in Scheme I only for simplicity. The spectrum shown in Figure 1 is that of the *threo*-9 actually obtained starting from *threo*-1. These experiments were carried out by Dr. D. J. Boschetto and are included here with his tacit permission: cf. D. J. Boschetto, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1971, and ref 4.

(22) B. Sjoborg and S. Herdevall, *Acta Chem. Scand.*, 12, 1347 (1958).

(23) We wish to thank our colleagues Rudy Lauer and Barry Sharpless for a gift of diphenyl diselenide and for advice on the preparation of alkyl phenyl selenides.

(24) G. N. Schrauzer, *Inorg. Syn.*, 11, 61 (1968).

prepared using a literature procedure.[17] Finely chopped lithium wire (0.18 g, 28 mg-atoms) and 5 ml of dried, degassed THF were placed in a flame-dried 25-ml flask equipped with a magnetic stirring bar and a nitrogen inlet. The reaction vessel was cooled in a 25° water bath and rapid stirring was initiated. A solution of 0.80 g (4.0 mmol) of trimethyltin chloride in 5 ml of degassed THF was added slowly by cannula. The solution started to turn green after 5 min, and the reaction mixture was allowed to stir for 3 hr. The solution was filtered under nitrogen through glass wool, the filtrate was cooled to 0° (ice), and 0.60 g (3.64 mmol) of a 90:10 mixture of *erythro*- and *threo*-1-bromo-3,3-dimethylbutane-*1,2-d_2*[3] was added in drops. After an hour of additional stirring, the reaction mixture was hydrolyzed with 10 ml of H_2O and extracted with three 5-ml portions of ether. The combined extracts were dried ($MgSO_4$) and all material boiling below 100° was distilled through a 10-cm Vigreux distillation column, leaving 0.43 g (1.79 mmol, 49%) of crude product. A sample of this material was purified by glpc using a 0.25-in. UCW-98 column held at 125° and had: ir (CCl_4) 2950, 1580, 1480, 1370, 1245, 1070, 1020, 685 cm^{-1}; deuterium-decoupled nmr (CDCl₃) δ 0.03 (s, 9), 0.84 (s, 9), 1.24 (two overlapping doublets,

1, J = 4.2 Hz and 14.2 Hz in ratio of 3:1). The doublets at δ 0.67 were partially obscured.

threo-3,3-Dimethylbutyl-*1,2-d_2*-mercuric Chloride (9). To a solution of 349 mg (1.3 mmol) of cyclopentadienyl(*threo*-3,3-dimethyl-butyl-*1,2-d_2*)dicarbonyliron in 15 ml of benzene was added 360 mg (1.3 mmol) of mercuric chloride. The resulting suspension was stirred for 4 hr at 40° under nitrogen. An ir spectrum of an aliquot of the resulting red solution indicated that carbonyl bands at 2005 and 1955 cm^{-1} characteristic of the starting alkyliron compound had completely disappeared and had been replaced by new bands at 2000 and 2025 cm^{-1} due to cyclopentadienyldicarbonyliron chloride. The benzene was removed under reduced pressure and the residue extracted with hot ethanol. The ethanol solution was allowed to crystallize at room temperature to afford 96 mg (23%) of 9 as white crystals, mp 132–134° (lit.[25] mp 132–132.4°). The nmr spectrum of 9 (CDCl₃) consisted of peaks at δ 0.73 (9H, s), 1.75 (1H, d, J = 5.2 Hz), and 1.25 (1H, d, J = 5.2 Hz).

(25) G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Amer. Chem. Soc.*, 89, 1135 (1967).

Copper(I) Alkoxides. Synthesis, Reactions, and Thermal Decomposition[1]

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Abstract: Alkoxides and phenoxides of copper(I) can be prepared by the heterogeneous reaction between alcohols and phenols and methylcopper(I). These organocopper(I) compounds are useful reagents for the formation of ethers by displacement of halide from organic halides. The reaction of copper(I) alkoxides with aryl halides yields alkyl aryl ethers under particularly mild conditions. Thermal decomposition of primary alkoxycopper(I) reagents generates intermediate alkoxy radicals. Thermal decomposition of secondary alkoxycopper(I) reagents apparently can take place either by a free-radical mechanism or by a mechanism tentatively suggested to involve copper(I) hydride as an intermediate. The structural factors determining which mechanism will predominate for a given compound have not been established.

The utility of alkyl- and arylcopper(I) reagents in organic synthesis is based on their high nucleophilicity toward carbon, and on their ability to take part in electron-transfer reactions.[2–4] They also show low basicity toward protons, an affinity for carbon–carbon double bonds, and an ability to coordinate with soft Lewis bases. Since the mechanisms by which copper(I) influences the reactivity of carbanions are not clearly understood, it is difficult to predict the behavior of new types of organocopper(I) compounds. Nevertheless, there is obvious reason to hope that organic derivatives of copper(I) other than those belonging to the well-explored class of compounds containing carbon–copper bonds might also show useful

reactivity. This paper describes studies of one such class: alkoxides of copper(I). These studies had three objectives: synthesis and characterization of alkoxides and phenoxides of copper(I); determination of the behavior of these substances in reactions whose usefulness with alkylcopper reagents has already been established; and examination of the mechanisms of their thermal decomposition.

Copper(I) alkoxides and phenoxides have been implicated previously as intermediates in a variety of copper-catalyzed reactions,[4,5] and poorly characterized examples of these substances have been prepared.[6] A useful synthesis of copper(I) *tert*-butoxide[7] is not applicable to the preparation of the thermally unstable copper(I) primary and secondary alkoxides that were of central interest in our work. The preparation of copper(I) phenoxide by a procedure analogous to that described here has been reported.[8] Copper(I) alkoxides

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

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(3) G. Bähr and P. Burba in "Methoden der Organischen Chemie" (Houben-Weyl), Vol. XIII/1, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1970, p 731 ff.

(4) O. A. Chaltykian, "Copper-Catalytic Reactions," A. E. Stubbs, trans., Consultants Bureau, New York, N. Y., 1966; P. E. Fanta, *Chem. Rev.*, 64, 613 (1964); R. G. R. Bacon and H. A. O. Hill, *Quart. Rev., Chem. Soc.*, 19, 95 (1965); J. Peisach, P. Aisen, and W. E. Blumberg, Ed., "The Biochemistry of Copper," Academic Press, New York, N. Y., 1966.

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(8) T. Kawaki and H. Hashimoto, *Bull. Chem. Soc. Jap.*, 45, 1499 (1972).