H), 3.08 (br q, $J = 7.2$ Hz, 1 H), 3.34–3.57 (m, 1 H), 3.73 (s, 3 H), 3.85 (s, 2 H, D_2O/KOD exchange), 4.10 (q, $J = 7.0$ Hz, 2 H), 5.77–5.95 (m, 2 H).

32c: oil; IR ($CHCl_3$) 1730 cm^{-1}; ^1H NMR δ 1.23 (t, $J = 7.0$ Hz, 3 H), 1.45 (s, 3 H), 1.78 (s, 3 H), 2.99 (br s, 2 H), 3.47 (br d, $J = 6.7$ Hz, 1 H), 3.72 (s, 3 H), 3.89 (s, 2 H, D_2O/KOD exchange), 4.11 (q, $J = 7.0$ Hz, 2 H), 5.49–5.83 (m, 1 H).

8a-Hydroxy-2-methoxy-4a-methyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinones (34a,b). A mixture of **33a** (190 mg, 0.8 mmol) and silica gel (3 g) in $CHCl_3$ (10 mL) was allowed to stand at room temperature for 3 days. The mixture was filtered and the silica gel was washed well with $CHCl_3$. The combined filtrates were concentrated and the residue was chromatographed on silica gel with $CHCl_3$ to give **34a** (143 mg, 80%) as colorless crystals: mp 211–214 °C; IR ($CHCl_3$) 3600, 3400, 1725, 1675, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (s, 3 H), 2.13–2.43 (m, 2 H), 2.21 (s, 1 H, D_2O exchange), 2.71 (d, $J = 20.7$ Hz, 1 H), 3.81 (s, 3 H), 5.60–5.80 (m, 2 H), 5.86 (s, 1 H); MS, m/e 222 (M^+).

Anal. Calcd for $C_{12}H_{14}O_4\cdot{}^1/_{10}H_2O$: C, 64.33; H, 6.39. Found: C, 64.09; H, 6.25.

The similar silica gel treatment of **33b** afforded **34b** in 36% yield: mp 175–178 °C; IR ($CHCl_3$) 3570, 3400, 1720, 1665, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (s, 3 H), 1.70 (br s, 6 H), 2.03–2.98 (m, 4 H), 2.17 (s, 1 H, D_2O exchange), 3.81 (s, 3 H), 5.85 (s, 1 H).

General Procedure for Acid-Catalyzed Reaction of Adducts. To a stirred solution of the appropriate adduct (1 mmol) in anhydrous methanol or ethanol (5 mL) at 0 °C was added one small drop of acetyl chloride. After stirring at room temperature for 20 h, the mixture was concentrated in vacuo and the residue was chromatographed on silica gel with a $CHCl_3$/MeOH solvent system to give the pure product (the yields are given in text). The physical properties and spectroscopic data of these products are summarized in Table II.

1-Acetoxy-4-methoxy-4a-methyl-5,8-dihydro-2(4a*H*)-naphthalenone (36). A solution of **35a** (62 mg, 0.3 mmol) in a 1:1 mixture of acetic anhydride and pyridine (1 mL) was stirred at room temperature for 30 min. The usual workup and chromatography on silica gel afforded **36** (58 mg, 78%) as colorless crystals: mp 91–93 °C (ether/n-hexane); IR ($CHCl_3$) 1775, 1680, 1650, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (s, 3 H), 2.29 (s, 3 H), 2.18 (dm, $J = 16.5$ Hz, 1 H), 2.56 (dm, $J = 16.5$ Hz, 1 H), 2.80 (dm, $J = 20.0$ Hz, 1 H), 3.22 (dm, $J = 20.0$ Hz, 1 H), 3.75 (s, 3 H), 5.59 (s, 1 H), 5.64–5.78 (m, 2 H). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.54; H, 6.45.

Acknowledgment. We are grateful to Y. Okamoto (Kyhushu University) for the preparation of 1,4-benzoquinones **19–21**.

Registry No. 1, 614-13-1; **2a**, 689-89-4; **2b**, 2396-84-1; **2c**, 13369-24-9; **3a**, 90454-41-4; **3b**, 90454-42-5; **3c**, 90454-45-8; **5**, 90454-43-6; **6a**, 96040-58-3; **6b**, 96040-59-4; **8a**, 96040-60-7; **8b**, 96040-61-8; **9**, 96040-62-9; **10**, 90454-44-7; **15a**, 92173-45-0; **15b**, 96040-63-0; **16a**, 96040-64-1; **16b**, 96040-65-2; **17**, 96040-66-3; **18**, 96040-67-4; **19**, 2880-58-2; **21**, 90111-21-0; **22**, 96040-68-5; **23**, 96040-69-6; **24**, 52280-68-9; **27**, 58822-93-8; **28**, 96055-50-4; **29**, 96055-51-5; **30**, 96040-70-9; **31a**, 90454-48-1; **31b**, 90454-49-2; **31c**, 96040-71-0; **32a**, 90454-47-0; **32b**, 90454-46-9; **32c**, 96040-72-1; **33a**, 96040-73-2; **33b**, 96040-74-3; **34a**, 96040-75-4; **34b**, 96040-76-5; **35a**, 96040-77-6; **35b**, 96040-78-7; **36**, 96040-79-8; **37**, 96040-80-1; guaiacol, 90-05-1; m-cresol, 108-39-4; 5-methyl-2-(methylthio)phenol, 23385-54-8; 1,3-butadiene, 106-99-0.

Notes

Organoboranes in Organic Synthesis: Reactions of Homo- and Heterocuprates with 9-Borabicyclo[3.3.1]nonane

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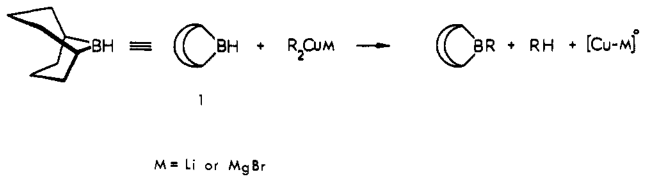
Received August 10, 1983

For sometime we have been investigating the reaction of various lithium and halomagnesium dialkylcuprates with organoboranes[1,2] (Scheme I). The advantage of this method enables the synthesis of certain organoboranes (B-methyl, B-aryl, B-1-ethynyl, B-neopentyl, B-benzyl) which cannot be prepared via the normal hydroboration of carbon–carbon multiple bonds. The published preparation of such organoboranes involves a two-stage procedure and certain protic reagents or Lewis acids (CH_3SO_3H, CH_3OH, HCl, $BF_3(CH_3CH_2)_2O$.[3-5] Our method overcomes the use of these reagents and allows the new synthesized organoboranes to be used for further proton-sensitive reactions.

Despite this convenience of having the new organoborane generated in situ, a disadvantage is that only one of the alkyl groups of the cuprate is utilized, a problem if such cuprates are difficult to prepare or involve expensive starting materials.

Scheme I



Certain workers[6-7] have reported the use of homo- and heterocuprates in reactions with various electrophiles where the valuable alkyl group (Rt) is selectively transferred to the electrophile leaving the dispensable residual (Rr) attached to the copper metal. This appears most pronounced when the copper (I) derivative of the residual group [(Rr)Cu] is particularly stable (eq 1).

$$(Rt)(Rr)CuM + E^+ \rightarrow (Rt)E + [(Rr)Cu] + M^+ \quad (1)$$

$$Rr = n\text{-BuC}{\equiv}\text{C},\ n\text{-PrC}{\equiv}\text{C},\ t\text{-BuC}{\equiv}\text{C},\ t\text{-BuO, PhO, PhS}$$

$$M = \text{Li, MgBr}$$

We now report the reaction of various homo- and heterocuprates with 9-borabicyclo[3.3.1]nonane (9-BBN, **1**).

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[1] Whiteley, C. G. *J. Chem. Soc.*, Chem. *Commun.* **1981**, 5.
[2] Whiteley, C. G. *S. Afr. J. Chem.* **1982**, *35*, 9.
[3] Hubbard, J. L.; Kramer, G. W. *J. Organomet. Chem.* **1978**, *156*, 81.
[4] Sinclair, J. A.; Molander, G. A.; Brown, H. C. *J. Am. Chem. Soc.* **1977**, *99*, 954.
[5] Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1.
[6] Posner, G. H.; Whitten, C. E.; Sterling, J. J. *J. Am. Chem. Soc.* **1973**, *95*, 7788.
[7] Mandeville, W. H.; Whitesides, G. M. *J. Org. Chem.* **1974**, *39*, 400.
[8] Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210.

Table I. Reaction of Homo- and Heterocuprates with 9-BBN

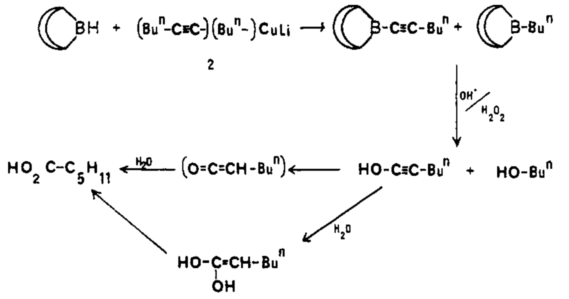
entry	Rr	Rt	M	oxidation[a] products	(yield),[b] %)
1	n-BuC≡C	Me	Li	MeOH (43)	$C_5H_{11}COOH$ (35)
2	n-BuC≡C	n-Bu	Li	n-BuOH (38)	$C_5H_{11}COOH$ (33)
3	n-BuC≡C	n-Pr	MgBr	n-PrOH (38)	$C_5H_{11}COOH$ (30)
4	PhO	n-Bu	Li	n-BuOH (65)	
5	PhO	t-Bu	Li	t-BuOH (60)	
6	PhO	n-Pr	MgBr	n-PrOH (66)	
7	t-BuO	n-Bu	Li	n-BuOH (10); t-BuOH (85)	

[a] *cis*-1,5-Cyclooctanediol is also produced. [b] By GC analysis.

Table II. Reaction of (Phenylthio)alkylcuprates (PhS)(Rt)CuM with 9-BBN

entry	Rt	M	oxidation[a] products	yield, %
8	Me	Li	MeOH	92
9	Ph	MgBr	PhOH	77
10	$PhCH_2$	MgBr	$PhCH_2OH$	67
11	n-Bu	Li	n-BuOH	86
12	t-Bu	Li	t-BuOH	83
13	n-Pr	MgBr	n-PrOH	90

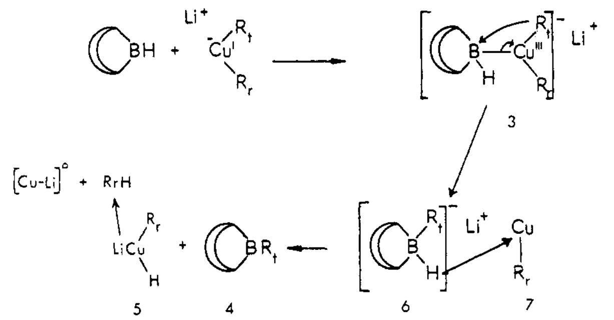
Scheme II



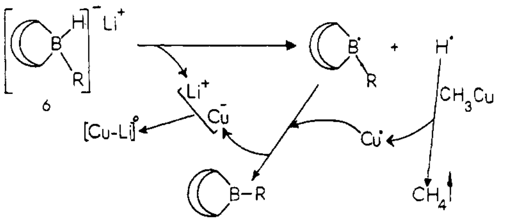
Our results are shown in (Tables I and II). We chose 9-BBN because of its availability, remarkable physical and chemical characteristics, insensitivity to air, thermal stability, and solubility in a variety of organic solvents.[9] *B*-Alkyl-9-BBN compounds have shown considerable utility in organic synthesis.[10]

An ethereal solution of 1-hexynylbutylcopper lithium (**2**) was treated with 9-BBN (1 equiv) at −80 °C and the whole allowed to reach room temperature. At approximately −40 °C the reaction mixture gradually darkened with a concomitant evolution of gas, and after 18 h at room temperature a brilliant copper mirror had formed, leaving a clear, colorless supernatant solution. The volatiles were removed under reduced pressure and the residue was oxidized in the usual manner[11] (5 M NaOH; 30% H_2O_2). Continuous ether extraction of the chocolate brown heterogeneous mixture afforded 1-butanol (38% yield).[12] The yields were somewhat disappointing since previous studies[1,2] had produced far more favorable results. When the aqueous brown solution was acidified and further extracted with ether, a compound identified as hexanoic acid was isolated.[13] It was evident, though unexpected, that both the alkyl and alkynyl groups were transferred (Scheme II). We believe that α-hydroxyacetylenes may either be hydrated to the enol form before tautomerism to the corresponding acid or that there is an initial tautomerism producing a ketene which is then hydrolyzed to the acid.

Scheme III



Scheme IV



In terms of the mechanism for the reaction of electrophilic species with organocuprates,[14] we believe that there are two possibilities. Firstly, there is an initial oxidative addition step to produce a copper(III) intermediate (**3**) [Scheme III]. This is followed by a reductive elimination step with the transfer of one of the groups producing a *B*-alkyl-9-BBN hydride (**6**) and the corresponding alkyl copper (**7**). Lithium trialkylborohydrides are well-known as reducing agents and a potent source of hydride ions.[15] We suggest that there is disproportionation and the hydride shifts to the copper metal to form a lithium hydridocuprate (**5**) and the organoborane **4**. It is this cuprate which thermally decomposes, releasing hydrogen, oxidative coupled product (Rr–Rr), or Rr–H and depositing a copper mirror.[16]

A radical mechanism may also explain the observed results (Scheme IV).[17] Transition-metal ions are capable of both donating and accepting single electrons.[18] Thus it is assumed that **6** donates an electron to methylcopper, releasing the alkane and thus allowing electron transfer to take place to produce the organoborane and a copper–lithium amalgam. Although the evidence does not exclude either of these mechanisms, the difficult nucleophilic reaction of a hydride ion of **6** with **7** (R = n-BuC≡C, Ph) must favor a radical-type reaction.

It was reported[19] that acetylenic ligands are tightly bound to the copper metal through π*–p or π*–d orbital overlap. However, with the initial oxidative addition copper(III) complex **3** (Scheme III) (Rr = n-BuC≡C; Rt = n-Bu), this mutual overlap is decreased in favor of electron donation from the copper metal to the electro-

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[9] Brown, H. C.; Lane, C. F. *Heterocycles* **1977**, *7*, 453.

[10] Scouten, C. G.; Brown, H. C. *J. Org. Chem.* **1973**, *38*, 4092.

[11] Brown, H. C. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

[12] By GC analysis.

[13] The possibility that hexanoic acid was an artefact arising from alkaline peroxide reaction of unreacted 1-hexyne was discarded. Such a reaction on authentic 1-hexyne returned the alkyne unchanged.

[14] Pelter, A.; Smith, K. in "Comprehensive Organic Chemistry"; Neville-Jones, D., Ed.; Pergamon Press: Oxford, England, 1979; Vol. 3, p 689.

[15] Gladysz, J. A. *Aldrichimica Acta* **1979**, *12*, 13.

[16] See: House, H. O.; Dubose, J. C. *J. Org. Chem.* **1975**, *40*, 788 and references sited therein.

[17] Davies, A. G.; Roberts, B. P. *Acc. Chem. Res.* **1972**, *5*, 387.

[18] Stirling, C. J. "Radicals in Organic Chemistry"; Olbourne Press: London, 1965; p 61.

[19] Gordon-Gray, C. G.; Whiteley, C. G. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2040.

philic boron atom. This must allow the transfer of both the alkyl and the alkynyl groups to the boron atom (Scheme II).

Our attention turned to using the various mixed heterocuprates (Rr = PhS, PhO, or *t*-BuO). In these cases we would expect stronger σ–p/σ–d orbital overlap between the heteroatom and the copper metal. Thus we envisaged that such groups would remain attached to the copper leaving the alkyl group (Rt) to be transferred.

The mixed heteroalkylcuprates were prepared[6] and treated at −80 °C with 1 equiv of 9-BBN. Though tetrahydrofuran offered a more homogeneous solution in comparison to ether as solvent, no advantages in the overall yield were forthcoming. As the solutions warmed to about −40 °C, they darkened, eventually (18 h, room temperature) depositing black colloidal copper and leaving a clear supernatant. In the case of (phenylthio)alkylcuprate, very little black colloidal copper precipitated, which implied marked stability of the lithium (phenylthio)hydridocuprate (**5**)[20] (Scheme III, Rr = PhS). Substantially more copper metal deposit came from the use of lithium phenoxyalkylcuprate (entries 4, 5, 6; Table I), again reflecting, to a lesser extent, the thermal stability of the phenoxyhydridocuprate. With lithium *tert*-butoxyalkylcuprate a, definite copper mirror formed. This and the poor yield from alkyl transfer to the boron atom (entry 7; Table I) pointed to a preferential thermal decomposition of the heterocuprate rather than allowing selective transfer of the alkyl group.

The alkylated 9-BBN products **4** (Scheme III) were not isolated but instead subjected to oxidation. The results showed high-yield transfer of the alkyl group with lithium (phenylthio)alkylcuprates (Table II), moderate reaction with lithium phenoxyalkylcuprates (entries 4, 5, 6 Table I), and somewhat disappointing results with lithium *tert*-butoxyalkylcuprate (entry 7, Table I).

Posner et al.[6] reported a similar stability/reactivity temperature profile. At −50 °C all three heterocuprates were stable; at −30 °C the *tert*-butoxycuprate had decoposed, leaving (phenylthio)- and phenoxycuprates as viable species, and at 0 °C only the (phenylthio)cuprate remained stable and reactive. The limiting factor in our case is the temperature of reaction of the lithium heteroalkylcuprate with 9-BBN. At −40 °C lithium *tert*-butoxyalkylcuprate decomposes rapidly, leading to very little alkylation of the organoborane (entry 7, Table I). On the other hand, lithium (phenylthio)alkylcuprate is thermally stable at 0 °C, which allows virtually complete transfer of the alkyl group to form the product in high yield (Table II). Practical utilization of homo- and heterocuprates necessitates overcoming several limitations as well as requiring a balance between selectivity and reactivity. The reaction of mixed (phenylthio)alkylcuprates with 9-BBN described here overcomes the problems associated with (a) the thermal instability of phenoxy- and *tert*-butoxyalkylcuprates, (b) the low reactivity of mixed acetylenic cuprates, and (c) the wasting of one R group of the homocuprates R_2CuLi.

Experimental Section

General Procedures. Diethyl ether and tetrahydrofuran were refluxed for several hours over calcium hydride and then distilled, under nitrogen from lithium aluminum hydride, just prior to use. Solvents and air-sensitive materials were transferred to hypodermic syringe and double-ended needles according to known methods.[11] *n*-Butyllithium in hexane, *tert*-butyllithium in pentane, and methyllithium in ether were commercial products (Aldrich). The alkyllithium reagents were standardized according to the procedure of Watson and Eastham[21] using 2,2-bipyridyl as the indicator. In the case of methyllithium a further standardization was performed at −35 °C. Propylmagnesium bromide was prepared by known methods[22] and standardized by using biquinolyl as indicator. Copper(I) iodide (Merck) was continuously extracted with tetrahydrofuran in a Soxhlet apparatus (48 h) and dried in vacuo at 20 °C. All reactions were performed in a two-necked cylindrical flask, equipped with serum stoppers under a static source of dry nitrogen. Prior to the introduction of solvents, the apparatus was charged with copper(I) iodide and flamed while being evacuated and then allowed to cool under a stream of dry nitrogen. 1-Hexyne was distilled (70–71 °C) under nitrogen and stored over molecular sieves (4 Å) at 0 °C. Thiophenol, phenol, and *tert*-butyl alcohol were obtained from commercial sources and used without further purification. 9-Borabicyclo[3.3.1]nonane was purchased (Aldrich) as a 0.5 M solution in tetrahydrofuran. Alcohols were detected on a Perkin-Elmer 900 gas chromatograph (flame ionization detector) using 3 ft × $^1/_8$ in. 15% HIEFF 4BP on Chromosorb Q.

Halomagnesium and Lithium (1-Hexynyl)alkylcuprate. Preparation and Reaction with 9-BBN. To a solution of 1-hexyne (1.14 mL, 10.0 mmol) in ether (50 mL) at 5 °C was added *n*-butyllithium (4.4 mL, 2.29 M, 10.0 mmol), and the orange solution was stirred for 30 min. The mixture was then added to a suspension of copper iodide (1.9 g, 10.0 mmol) in ether (30 mL) at 0 °C and the whole was stirred for a further 1 h at this temperature. The canary-yellow mixture containing 1-hexynylcopper was cooled to −35 °C before being treated with the appropriate organometallic reagent (10.0 mmol).[23] After the hexynylalkylcuprate was stirred at −35 °C for 30 min, the solution was cooled to −78 °C, treated with 9-BBN (20 mL, 0.5 M, 10 mmol), and then allowed to reach room temperature. At −40 °C a black colloidal suspension of copper began to form which transformed into a brilliant copper mirror after stirring for 18 h at 20 °C. The solvents were stripped under reduced pressure, and aqueous sodium hydroxide (25 mL, 5 M) and hydrogen peroxide (25 mL, 30%) were added simultaneously at 0 °C; the temperature was then raised to 60 °C for 2 h. The chocolate-brown suspension was continuously extracted into ether, and GC estimation of the extract revealed the presence of the corresponding alcohol.[24] The aqueous solution was acidified and again continuously extracted into ether. Drying (Na_2SO_4) and evaporation of the ether layer produced hexanoic acid, identical with an authentic sample.

Lithium Thiophenoxide, Lithium Phenoxide, and Lithium *tert*-Butoxide.[6] Thiophenol (1.02 mL, 10.0 mmol) in tetrahydrofuran (25 mL) was treated with *n*-butyllithium (6.1 mL, 1.64 M, 10.0 mmol) at 0 °C under nitrogen, and the solution of lithium thiophenoxide used within 30 min. Lithium phenoxide and lithium *tert*-butoxide were prepared by similar procedures.

Representative Reaction of 9-BBN with Mixed Heterocuprates. A mixture of copper(I) iodide (1.9 g, 10.0 mmol) and dry tetrahydrofuran (50 mL) was cooled to 0 °C and treated with lithium thiophenoxide (10.0 mmol). This solution was stirred for 30 min and then cooled to −80 °C, and *tert*-butyllithium (4.8 mL, 2.1 M, 10.0 mmol) was added slowly. After a further 30 min at this temperature, 9-BBN (20 mL, 0.5 M, 10.0 mmol) was added, and the whole was allowed to reach room temperature. No copper mirror deposited. The volatiles were removed under reduced pressure and the residue was oxidized by adding, at 0 °C, aqueous sodium hydroxide (25 mL, 5 M) and hydrogen peroxide (25 mL, 30%); the temperature was then raised to 60 °C for 2 h. The aqueous layer was continuously extracted into ether and GC estimation of the extract revealed the presence of *tert*-butyl alcohol (83%).[24]

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(20) Quenching of the solution of **5** with aqueous ammonium chloride resulted in the formation of a yellow suspension of (phenylthio)copper.

(21) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(22) Vogel, A. "Textbook of Practical Organic Chemistry"; Longmans: New York, 1978.

(23) With methyllithium (entry 1, Table I) it was found, by titration at −35 °C, that the concentration of alkyl lithium was reduced by one-third. This may be due to the formation of cross-associated species Me_3Li_4Br in ether.[25] Additional alkyl lithium was, therefore, added accordingly.

(24) *cis*-1,5-Cyclooctanediol was also produced.

(25) Novak, D. P.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, *94*, 3793.

Acknowledgment. We are grateful for financial support from the Council for Scientific and Industrial Research, Pretoria.

Registry No. 1, 280-64-8; 2, 62197-73-3; (n-BuC≡C)(Me)CuLi, 41799-09-1; (n-BuC≡C)(n-Pr)CuMgBr, 95765-20-1; (PhO)(n-Bu)CuLi, 95765-21-2; (PhO)(t-Bu)CuLi, 50281-68-0; (PhO)(n-Pr)CuMgBr, 95765-23-4; (t-BuO)(n-Bu)CuLi, 41655-89-4; MeOH, 67-56-1; n-BuOH, 71-36-3; n-PrOH, 71-23-8; t-BuOH, 75-65-0; $C_5H_{11}COOH$, 142-62-1; (PhS)(Me)CuLi, 56831-21-1; (PhS)(Ph)CuMgBr, 95765-25-6; (PhS)($PhCH_2$)CuMgBr, 95765-27-8; (PhS)(n-Bu)CuLi, 53128-68-0; (PhS)(t-Bu)CuLi, 50281-66-8; (PhS)(n-Pr)CuMgBr, 95765-29-0; PhOH, 108-95-2; $PhCH_2OH$, 100-51-6; n-BuC≡CH, 693-02-7; n-BuC≡CCu, 33589-44-5; PhSH, 108-98-5; PhSLi, 2973-86-6; PhOLi, 555-24-8; t-BuOLi, 1907-33-1; *cis*-1,5-cyclooctanediol, 23418-82-8.

A Simple Procedure for Stereospecific Vicinal Dicarboxylation of Olefins

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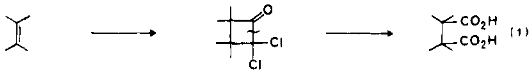
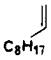
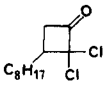
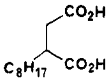
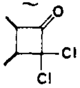
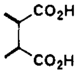
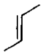
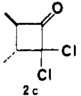
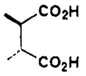
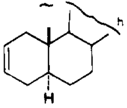
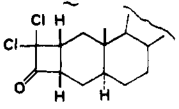
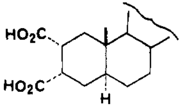
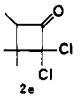
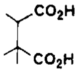
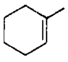
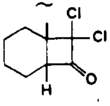
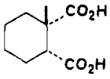
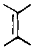
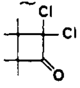
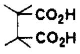
Recently, we required a method for effecting vicinal dicarboxylation or dicarbalkoxylation of a trisubstituted olefin and were unable to find any suitable procedures in the literature. The best known method for effecting this kind of transformation is the palladium-catalyzed carbonylation reaction; however, this is very limited in scope, being applicable only to certain types of mono- and disubstituted olefins.[1]

Our interest in the chemistry of α,α-dichlorocyclobutanones[2] led us to consider the possibility of effecting dicarboxylation through the intermediacy of the dichloroketene–olefin cycloadducts[3] (eq 1). In this note we offer a straightforward procedure based on such an approach.


(1)

In a few cases, cleavage of the $-CCl_2CO-$bond of these cycloadducts to give potentially useful intermediates has been possible through reaction with alkoxides or amines;[3a,d,4] most often, though, the products from these and similar treatments are those resulting from cleavage of the other carbon–carbonyl bond, ring contraction, and ring expansion (processes involving cine displacement).[3d,5]

Table I. Vicinal Dicarboxylation of Olefins

olefin	dichloro-cyclobutanone	yield[a]	succinic acid	yield
 **1a**	 **2a**	88%[b]	 **3a**	94%[c]
 **1b**	 **2b**	79%[d]	 **3b**	78%[e]
 **1c**	 **2c**	80%[f]	 **3c**	76%[g]
[h] **1d**	 **2d**	[i]	 **3d**	73%[f,j]
 **1e**	 **2e**	87%[k]	 **3e**	75%[l]
 **1f**	 **2f**	83%[m]	 **3f**	93%[n]
 **1g**	 **2g**	61%[m]	 **3g**	86%[o]

[a] Yield of distilled product based on olefin (**2a,f**) or reagent (**2b,c,e,g**). [b] Reference **2a**. [c] mp 87 °C (lit.[1d,15] mp 90 °C). Lithium dimethylcopper was used.[12] [d] Reference 10. [e] mp 199 °C dec [lit.[16] mp 209 °C (198 °C dec)]. [f] See Experimental Section. [g] mp 128 °C (lit.[16] mp 129 °C). [h] 5α-Cholest-2-ene.[9] [i] Reference 11. Crude product used in next step. [j] Yield based on **1d**. [k] Reference 3c. [l] mp 146 °C (lit.[17] mp 152 °C). [m] References 3b,c. [n] mp 156–157 °C (lit.[18] mp 159.5–161 °C). [o] mp 196 °C (lit.[19] mp 200 °C).

Instead of searching for other nucleophiles that might more generally attack the carbonyl, we sought to profit from an earlier observation that the α,α-dichlorocyclobutanones, in most cases, can be cleanly converted to the corresponding α-chloro enolates merely through treatment with n-butyllithium.[6] While we were unsuccessful in finding a high-yield method for directly oxidizing the enolates to succinic acids, an efficient, normally one-pot procedure was found for carrying out the desired cleavage via these enolates, viz., through successive treatment of the α,α-dichlorocyclobutanones with n-butyllithium, acetic anhydride, and sodium metaperiodate–ruthenium dioxide.[7] Examples of the vicinal dicarboxylation are given in Table I.

The *overall* yields for the dicarboxylation range from 52% to 83% and average 68%. Not unexpectedly,[8] the conversion is totally stereospecific: **1b** yields only **3b** and **1c** gives only **3c**. Finally, in that lithium dimethylcopper can be used in place of n-butyllithium,[2b,c] the procedure can accommodate certain additional functional groups, as illustrated in eq 2.

We expect that this dicarboxylation method will prove useful due to its simplicity, generality, and high yields.

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