to room temperature, whereupon it was poured into ice with stirring and then ether was added. The ether, water, and solid phases were separated, and the water phase was extracted with ether. The solid was washed repeatedly with ether, and the ether phases were combined, dried, and concentrated. The dark residue was sublimed to give yellow crystals. These were washed with petroleum ether and recrystallized from chloroform–hexane to give 0.68 g of product with a melting point of 156–161 °C. Chromatography (chloroform–hexane) of the residue from the combined mother liquor and the petroleum ether washes followed by sublimation and recrystallization gave an additional 0.11 g: mp 155–161 °C; total yield 0.79 g (17%). Further recrystallization from chloroform–hexane gave a product melting from 160–161.5 °C: MS, *m/e* (relative intensity) M^+ 234 (9), 235 (8), 236 (22), 238 (46), 240 (15) (calcd relative intensity, 9, 7.5, 24, 50, 9, respectively); ^{1}H NMR δ 7.84 (4). Anal. Calcd for $C_5H_2S_3Se$: C, 25.32; H, 0.85. Found: C, 25.25; H, 0.87.

$\Delta^{2,2'}$-Bis(1,3-dithiolo[4,5-*c*]selenophene) (7). The thione 6 (0.60 g, 2.5 mmol) was heated under reflux in trimethyl phosphite (9 mL) in a nitrogen atmosphere. The reactant dissolved and a precipitate formed in 15 min. The reaction was continued for 1.75 h and then refrigerated. The product was collected by filtration and washed with ether, 0.25 g of 1 was obtained, and the melting point was 260–263 °C. Chromatography of the filtrate (silica gel, ethyl acetate) gave 30 mg of product, mp 256–262 °C, total yield 0.28 g (54%): MS (ionizing potential = 19 eV), *m/e* (relative intensity) M^+ 406 (6.2), 407 (4.8), 408 (15.3), 409 (10), 410 (26.0), 412 (base peak, 29.0), 414 (11.5) (calcd relative intensity, 4.7, 3.6, 14.8, 7.5, 25.6, 29.3, 9.0, respectively); ^{1}H NMR (Me_2SO-d_6) δ 7.97 (s). Anal. Calcd for $C_{10}H_4S_4Se_2$: C, 29.27; H, 0.99. Found: C, 29.65; H, 0.77.

$\Delta^{2,2'}$-Bithieno[3,4-*d*]-1,3-dithiole. Thieno[3,4-*d*]-1,3-dithiol-2-thione[7] (0.19 g, 1 mmol) was heated under reflux in a nitrogen atmosphere in 1.2 mL of trimethyl phosphite for 2 h, during which time a small amount of crystals had formed. After refrigeration, 0.05 g (32%) of crystals were obtained, mp 260–263 °C (lit.[9] mp 259–260 °C). Chromatography of the mother liquor gave a small amount of the product: MS, *m/e* 316 (M^+, base peak), 158 (M^{2+}).

Acknowledgment. R.K. was on sabbatical leave from UCSF. Financial support from the Swedish Natural Science Research Council to S.G. and A.-B.H. is gratefully acknowledged. The MS and NMR measurements were performed by Rolf Servin and Einar Nilsson.

Registry No. 1, 17422-59-2; 3, 88609-68-1; 4, 82451-15-8; 5, 88589-46-2; 6, 88589-47-3; 7, 88609-67-0; $\Delta^{2,2'}$-bithieno[3,4-*d*]-1,3-dithiole, 80229-45-4; thieno[3,4-*d*]-1,3-dithiol-2-thione, 80229-39-6; selenophene, 288-05-1; 3-bromoselenophene, 25109-24-4; 3-(methylthio)selenophene, 35577-04-9.

Dicyclohexylphosphide as an Auxiliary Ligand for Thermally Stable Heterocuprates with Considerably Improved Reactivity. Some Beneficent Effects of LiBr on Cuprate Reactivity

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Received July 18, 1983

Organocuprates, RR′CuLi, have been the most useful class of organometallic reagents for C–C bond formation developed during the past 2 decades and one of the most useful ever developed.[1] In spite of their importance, systematic comparisons of organocuprate stability and reactivity have not been undertaken until recently.[2] Such studies of thermal stability[3] have resulted in the development of new heterocuprates (R′ = PPh_2, NCy_2) that have the highest stability and still maintain high reactivity.[4] However, in some reactions these new cuprates were still too far away from our goal of a high yield with but 1.0 equiv of R. This is essential if cuprate reactions are to be used to make the key C–C bonds in convergent syntheses.[5] We have now found that the use of dicyclohexylphosphide (PCy_2) as the auxiliary ligand gives thermally stable cuprates with considerably improved reactivity. In the course of these studies, we observed that the presence of LiBr has a beneficent effect on the yields of product.

Results and Discussion

Organocuprates are generally prepared by adding an organolithium reagent to a Cu(I) halide such as CuI or $CuBr{\cdot}SMe_2$;[6] consequently, they contain 1 equiv of halide from the metathesis reaction (eq 1). Unless special steps

$$\mathrm{CuBr + RLi \rightarrow RCu + LiBr} \qquad (1)$$

$$\mathrm{RCu + R'Li \rightarrow RR'CuLi} \qquad (2)$$

are taken, the product of eq 2 contains the equivalent of LiBr from eq 1, whether the second lithium reagent added is RLi (homocuprate) or $LiPR_2$ (heterocuprate). Organic chemists generally ignore the fact that this LiBr is present.

For R = Me the preparation of halide-free cuprates is especially easy, since MeCu is extremely insoluble in ether or THF, allowing the ether-soluble Li halide to be extracted from it.[7] On the other hand, Me_2CuLi with extra equivalents of halide present can be obtained by using MeLi·LiBr or adding LiBr. The same expedients can be used to prepare the corresponding heterocuprates[8] containing various amounts of halide. The results of our studies, which utilized substrates representing four of the most important classes of synthetically useful cuprate reactions,[9] are summarized in Table I. Before detailing these results we emphasize that 1.0 equiv of $RCu(PCy_2)Li$ was used, rather than the 2–5-fold excesses of R_2CuLi commonly used.[10–12]

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(1) Posner, G. H. "An Introduction to Synthesis Using Organocopper Reagents"; Wiley: New York, 1980.

(2) For leading references to recent studies, see: (a) Lipshutz; B. H.; Parker, D.; Kozlowski, J. A.; Miller, R. D. *J. Org. Chem.* **1983**, *48*, 3334. (b) Johnson, C. R.; Dhanoa, D. S. *J. Chem. Soc., Chem. Commun.* **1982**, 358. (c) Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 192.

(3) Bertz, S. H.; Dabbagh, G. *J. Chem. Soc., Chem. Commun.* **1982**, 1030.

(4) Bertz, S. H.; Dabbagh, G.; Villacorta, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 5824.

(5) For example, in a number of convergent prostaglandin syntheses, the optically active (and therefore valuable) side chain is attached by using a homocuprate (R_2CuLi) to make the C(12)–C(13) bond; see ref 1, p 41, 43, 97.

(6) We have found this precursor to give superior results for both homocuprates and heterocuprates. In fact our phosphido cuprates cannot be prepared from CuI due to reduction to Cu.

(7) Casey, C. P.; Cesa, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4236. We used this procedure for halide-free MeCu with the following modifications: $CuBr{\cdot}SMe_2$ was used at 0 °C rather than $CuI(SBu_2)_2$ at −78 °C. When the MeCu thus obtained was hydrolyzed with H_2O, no LiBr was detected by $AgNO_3$ titration.

(8) For the reactions in Table I, the heterocuprates were prepared by using Method B of ref 4. See the Experimental Section.

(9) That our heterocuprates give high yields with an acid chloride is demonstrated by our thermal stability studies (ref 3 and 4). Allylic halides are more reactive than the alkyl halide we used here and would not have provided as challenging a test.

(10) Whitesides, G. M.; Fischer, W. F.; San Filippo, J.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871. Inspection of the data in Table IV of this paper reveals the same trend with increasing LiI that we observe with increasing LiBr.

0022-3263/84/1949-1119$01.50/0

Table I

				yield[a] (%) of product after		
entry	substrate	cuprate	equiv of LiBr	1 h/ −50 °C	25 °C 2 h	24 h
1	cyclohex-2-enone[b]	$MeCu(PCy_2)Li$	0	73	61	52
2			1	95	95	77
3			2	96	96	93
4		$BuCu(PCy_2)Li$	1	88	90	90
5			2[c]	88	88	89
6		$BuCu(NCy_2)Li$	1	60	62[d]	59
7			2[c]	67	61	63
8	1-iodooctane[e]	$MeCu(PCy_2)Li$	0	75	93	96
9			2	84	97	97
10		$MeCu(NCy_2)Li$	0	10	42	42
11			2	13	66	67
12		Me_2CuLi	0	75	100	100
13			2	100	100	100
14		$^1/_2Me_2CuLi$	2	7	19	22
15	cyclohexene oxide[f]	$MeCu(PCy_2)Li$	0	0	45	49
16			1	1	49	49
17			2	0	62	61
18			4[c]	2	64	62
19		$MeCu(PPh_2)Li$	1	0	28	35
20		$MeCu(NCy_2)Li$	0	0	4	21
21			2	0	17	49
22		Me_2CuLi	0	0	44	57
23			2	5	66	68
24		$Me_2Cu(CN)Li_2$	0	5	60	64
25			2	11	68	69
26	diethyl cyclopropane-1,1-dicarboxylate[g]	$MeCu(PCy_2)Li$	0	85	85	83
27			1	85	89	91
28			2	95	90	90
29		$BuCu(PCy_2)Li$	1	70	73	71
30			2	76	77	74

[a] Measured by GLC calibrated by using authentic products and internal standards. The reaction mixtures were prepared at −50 ± 3 °C, sampled after 1 h at this temperature, and then allowed to warm to 25 ± 2 °C. They were also sampled after 3 h (2 h out of the −50 °C bath) and 24 h. [b] With Me cuprates the product is 3-methylcyclohexanone, with Bu it is 3-butylcyclohexanone. [c] Solid LiBr was added to the $CuBr\cdot SMe_2$. [d] This yield was incorrectly reported as 92% in ref 4. [e] The product is nonane. [f] The product is *trans*-2-methylcyclohexanol. [g] With Me cuprates the product is diethyl propylmalonate, with Bu it is diethyl hexylmalonate.

Perusal of this table makes clear two important points: (i) the dicyclohexylphosphido ligand imparts excellent reactivity to heterocuprates (entries 1–5, 8–9, 15–18, 26–30) and (ii) the presence of LiBr significantly enhances the yield in a number of cases (entries 1–3, 8–13, 15–18, 20–23). Although it has been reported that lithium dimethylcuprate (1) prepared from methyllithium and copper(I) iodide appears to have the same reactivity toward alkyl halides as does pure 1,[10] we find an accelerating effect using the same substrate (1-iodooctane) and 1 prepared from $CuBr\cdot SMe_2$. Johnson et al.[11] have reported that ether is a better solvent than THF for the alkylation of epoxides. They proposed that the Li ion of the cuprate can be more effectively coordinated by the O atom of the epoxide in the less coordinating solvent. We reasoned that the same activating effect should be observed for LiBr (cf. next paragraph), which prompted our halide experiments. On the basis of the same sort of solvent effect, activation by the Li of Me_2CuLi has been proposed for the opening of 1,1-bisoxo cyclopropanes;[12] however, in the case of diethyl 1,1-cyclopropanedicarboxylate we see no effect of LiBr until 2 equiv are present and even then the effect is a modest one (entries 26–28). Krauss and Smith[13] have reported that the rates of cuprate additions to enones are retarded by LiI. In contrast, from a synthetic point of view, we find that Li halide dramatically improves the yield and the stability of the product from 1 and 2-cyclohexen-1-one (entries 1–3).

While the final yields in the halide displacements using $MeCu(PCy_2)Li$ or Me_2CuLi are independent of halide concentration (entries 8–9, 12–13), this is not the case for the epoxide openings. For $MeCu(PCy_2)Li$ the yield is up to 19% higher in the presence of halide (entries 15–18, 25 °C/2 h), and for Me_2CuLi the difference is as much as 22% (entries 22–23, 25 °C/2 h). In contrast the maximum difference is only 8% (entries 24–25) for Lipshutz's "higher order" $Me_2Cu(CN)Li_2$.[14] It should be noted that, while the highest yields for these three reagents are about the same (64%, 66%, and 68%, respectively), the latter two reagents require 2 equiv of R = Me; consequently, the yields per R are only half of that with the dicyclohexylphosphido reagent.

Of greater import for most synthetic applications, the yields based on substrate are, within experimental uncertainty (2–3%), as good as those obtained with the R_2 reagents. In this regard the dicyclohexylphosphidocuprates are much more reactive than previous thermally stable heterocuprates based on PPh_2 or NR_2.[3,4] Examples include the conjugate addition of Bu to 2-cyclohexen-1-one [90%

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(11) Johnson, C. R.; Herr, R. W.; Wieland, D. M. *J. Org. Chem.* **1973**, *38*, 4263.

(12) Yates, P.; Stevens, K. E. *Tetrahedron* **1981**, *37*, 4401. These authors prepared their reagent from CuI and MeLi·LiBr, thus it contained 2 equiv of Li halides. Therefore, their conjecture that chelation of a Li ion by the two oxo groups "may also account for the observation that two equivalents of the latter reagent [Me_2CuLi] were required for the reaction to proceed at a practicable rate" is probably not the case. We obtain better yields with 1 equiv of cuprate and an unhindered substrate. Steric hindrance may explain the low reactivity of their substrate.

(13) Krauss, S. R.; Smith, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 141.

(14) Lipshutz, B. H.; Kozlowski, J.; Wilhelm, R. S. *J. Am. Chem. Soc.* **1982**, *104*, 2305.

(entry 4) vs. 78% with $BuCuPPh_2Li$[4] and 67% with $BuCuNCy_2Li$ (entry 7)], the methylation of 1-iodooctane [97% (entry 9) vs. 57% with $MeCuPPh_2Li$[4] and 67% with $MeCuNCy_2Li$ prepared by method B[8] (entry 11) or 84% by method A[4]], and the methylation of cyclohexene oxide [64% (entry 18) vs. 35% with $MeCuPPh_2Li$[4] (entry 19) and 49% with $MeCuNCy_2Li$ (entry 21)]. The enhanced reactivity of cuprates containing the dicyclohexylphosphido ligand vis-a-vis the diphenylphosphido ligand[4] is attributable to the greater $+I$ effect of the cyclohexyl groups over that of the phenyl groups, making the former the better σ donor. The increased electron density on Cu, in turn, makes the transfer of the alkyl group from it more favorable.

In many ways, dicyclohexylphosphide is an ideal auxiliary ligand: it is commercially available, it is not difficult to handle by using conventional syringe techniques,[15] and it does not complicate workup procedures. The yields we obtain with the dicyclohexylphosphidocuprates are very reproducible and do not depend upon scale: a 90% yield (GLC) of 3-butylcyclohexanone from $BuCu(PCy_2)Li$ and 2-cyclohexen-1-one is observed on both 1-mmol and 50-mmol scale reactions. Both method A [$(LiPCy_2 + CuBr{\cdot}SMe_2) + RLi$] and method B [$(RLi + CuBr{\cdot}SMe_2) + LiPCy_2$] give the same yield, making the procedure extremely versatile. Isolated yields of 80% and 83% of analytically pure 3-butylcyclohexanone are obtained by chromatography and distillation, respectively, with no interference from phosphorus-containing byproducts after the usual aqueous workup (see Experimental Section). Tsuda et al.[2c] also report a 90% GLC yield and an 80% isolated yield of 3-butylcyclohexanone from their butyl(mesityl)copper(I) lithium and 2-cyclohexen-1-one. We believe our procedure to be more convenient, as most organic chemists are familiar with the preparation of lithium diisopropylamide (LDA), after which our preparation of $LiPCy_2$ is modelled.

In conclusion, dicyclohexylphosphide is the ligand of choice for mixed cuprates, imparting to them excellent reactivity as well as thermal stability. The yields that can now be obtained with 1.0 equiv of R are high enough to allow cuprate reactions to serve efficiently as the convergent steps in the synthesis of complex molecules.[16] The additional 10–20% improvements in yield observed when LiBr is present take on added significance when one considers the fact that cuprate reactions are commonly used in multistep syntheses where such an improvement in one step equals an improvement in the overall yield.

Experimental Section

General Information. Glassware was cleaned by washing it with concentrated nitric acid, concentrated ammonium hydroxide, distilled water, Alconox solution, distilled water, and finally acetone. Glassware was dried before use by heating it overnight in a 110 °C oven or for 1 min in a Bunsen burner flame. Flasks were cooled under nitrogen in a desiccator and purged with a strong stream of nitrogen before being fitted with rubber septa (Aldrich), or they were cooled and fitted with septa in a drybox. Syringe needles were washed with concentrated ammonium hydroxide, water, and acetone and then dried overnight in a 110 °C oven. Disposable syringes (B-D brand from SGA) were used, and the needles were sealed to them with a wrapping of Teflon brand tape. If necessary, syringes were cooled by holding them surrounded with dry ice in an insulated glove. All organocuprate reactions were run under an atmosphere of dry nitrogen admitted through the septa via syringe needles. The 1-mL disposable syringes may be connected to nitrogen lines after the tops are cut off. Reaction mixtures were stirred magnetically; Teflon-coated stirbars were cleaned with the same regimen used for glassware. Ether and THF were distilled as needed from sodium benzophenone ketyl and were transferred by syringe from the stillheads (Kontes) to the reaction flasks. With the use of good grades of ether (Mallinckrodt AR) and THF (Aldrich gold label) and by filling the stills via cannula, as many as 10 refills are possible before the pots (2-L round-bottomed flasks) need to be changed. Reagents were the best grade commercially available and were purified as necessary. Aqueous ammonium chloride solution (3 M) was deoxygenated by bubbling nitrogen through it for several hours before it was used.

Evaporation under reduced pressure was done on a Büchi Model RE apparatus with the solvent collection flask cooled in dry ice. GLC analyses were performed on a Hewlett-Packard 5880A gas chromatograph using 3 m × 3 mm nickel columns packed with 5% OV101 or 5% Carbowax 20M on Chromosorb W-HP (Alltech) and flame ionization detectors. A typical program was 65–200 °C at 10 °C/min. The HP-5880A was calibrated in the ISTD mode by using authentic products and internal standards (e.g., decane, dodecane, or tetradecane). NMR analyses were carried out with a JEOL FX-90Q NMR spectrometer; infrared spectra were obtained with a Nicolet 5DX FT-IR spectrometer. Microanalyses were performed by Galbraith Laboratories (Knoxville, TN).

Small-Scale Reactions (Typical Procedure). A 0.64-mL aliquot (1.00 mmol) of 1.56 M (0.09 M residual base) butyllithium (Aldrich, hexane solution) was added to a solution of 201 mg (1.02 mmol) of dicyclohexylphosphine (Aldrich) in 5.0 mL of dry, oxygen-free ether in a septum-sealed 25-mL pear-shaped flask cooled to −50 °C (dry ice/2-propanol bath). The reaction mixture was allowed to warm to ambient temperature (~23 °C) for 30 min. (In THF the maximum temperature was 0 °C.) The resulting suspension was cooled to −50 °C and transferred by cooled syringe (dry ice) into a suspension of butylcopper(I), prepared by adding 0.64 mL (1.00 mmol) of 1.56 M butyllithium to 206 mg (1.00 mmol) of copper(I) bromide–dimethyl sulfide complex (Aldrich) suspended in 5.0 mL of ether in a 25-mL recovery flask (Ace Glass, Inc.) at −50 °C and stirring the mixture for 15 min. The resulting phosphidocuprate was stirred for 15 min at −50 °C, and then a mixture of 96.7 mg (1.01 mmol) of 2-cyclohexen-1-one and 45.8 mg of tetradecane (internal standard) in 5.0 mL of ether in a septum-sealed 10-mL pear-shaped flask cooled to −30 °C was transferred into it via cooled syringe during 15 s. Samples (2.0 mL) were withdrawn after 1.0 h at −50 °C (cooled syringe), after the reaction mixture had been allowed to warm to ambient temperature (25 ± 2 °C) for 2.0 h (3.0-h total reaction time), and after 23 h at 25 °C (24 h total); they were quenched by injection into 2 mL of 3 M aqueous ammonium chloride in septum-sealed 2-dram vials. The organic layers were separated with disposable glass pipets and dried over anhydrous sodium sulfate (Baker granular) in 2-dram vials sealed with caps containing conical polyethylene inserts. Samples were stored in a freezer while awaiting GLC analysis.

3-Butylcyclohexanone (Method A). A 10.7-g (54.0 mmol) quantity of dicyclohexylphosphine (Aldrich) dissolved in 30 mL of dry, oxygen-free ether in a septum-sealed 100-mL pear-shaped flask was cooled to 0 °C (ice bath), and 37.5 mL (54.0 mmol) of 1.44 M (0.21 M residual base) butyllithium (Aldrich, in hexane) was added. The resulting suspension was stirred at 0 °C for 1 h and then transferred by cannula into a suspension of 10.9 g (53.0 mmol) of $CuBr{\cdot}SMe_2$ (Aldrich) in 60 mL of ether in a septum-sealed 500-mL round-bottomed flask, which was also at 0 °C. (The phosphide flask was rinsed with 10 mL of ether.) The homogeneous brown solution was stirred for 15 min at 0 °C and then cooled to −50 °C (dry ice/2-propanol bath) for 15 min. A 36.8-mL (53.0 mmol) quantity of 1.44 M butyllithium was added, and the homogeneous brown solution was stirred for 15 min at −50 °C. It was then cooled to −75 °C for 15 min, and 4.80 g (49.9 mmol) of 2-cyclohexen-1-one (Aldrich, distilled and refrigerated) in 20 mL of ether in a septum-sealed 50-mL pear-shaped flask cooled to −75 °C was added by cannula. (A further 5 mL of ether was used to rinse the 2-cyclohexen-1-one flask.) After 45 min at −75 °C, a 2.0-mL aliquot (out of a total of 200 mL) was withdrawn by syringe and added to 1 mL of 3 M aqueous ammonium chloride

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[15] Sasse, K. In "Methoden der Organischen Chemie (Houben-Weyl)"; Georg Thieme: Stuttgart, 1963; Vol. XII/1, p 14.

[16] Bertz, S. H. *J. Am. Chem. Soc.* **1982**, *104*, 5801.

in a septum-sealed 2-dram vial, which also contained 29.7 mg of tetradecane (internal standard). Calibrated GLC analysis indicated a 91% yield of product; no starting material remained. After a total of 1 h, 200 mL of 3 M aqueous ammonium chloride (deoxygenated with nitrogen) was added to the reaction mixture, which was allowed to warm to ambient temperature. The final pH of the aqueous layer was 8. The mixture was filtered through Celite 545, and the filter deposit was washed with 200 mL of ether. The organic layer was separated and back-extracted with 250 mL of 0.2 M aqueous sodium thiosulfate, 200 mL of ammonium chloride solution, 250 mL of 0.4 M aqueous sodium thiosulfate, and finally 100 mL of ammonium chloride. The aqueous layers were sequentially extracted with 50 mL of ether, which was added to the original organic layer. Drying over anhydrous sodium sulfate (Baker, granular) and evaporation under reduced pressure (<30 °C, 30 torr) gave 9.31 g of a yellow oil, which was purified by flash chromatography on 180 g of Florisil (Fisher) slurry-packed in a 3.5 × 40 cm column and eluted with 3.5 L of 5% ether/hexane followed by 0.5 L of 10% ether/hexane. All fractions collected were 50 mL (the column volume was 350 mL), and 5.61 g (98% pure by GLC) of product was recovered from fractions 11–76. An additional 0.53 g (98% pure) was obtained by stripping the column with 20% ether/hexane (~750 mL). The total yield of pure product was 6.14 g (80%).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.60; H, 11.59.

3-Butylcyclohexanone (Method B). A suspension of butylcopper(I) was prepared by adding 36.8 mL (53.0 mmol) of 1.44 M (0.21 M residual base) butyllithium (Aldrich, hexane solution) to a suspension of 10.9 g (53.0 mmol) of $CuBr{\cdot}SMe_2$ (Aldrich) in 60 mL of dry, oxygen-free ether in a septum-sealed 500-mL round-bottomed flask cooled to -50 °C. After the BuCu suspension had been stirred for 15 min at -50 °C, it was treated with a 0 °C suspension of lithium dicyclohexylphosphide, transferred by cannula from the septum-sealed 100-mL pear-shaped flask where it had been prepared by adding 36.8 mL (53.0 mmol) of 1.44 M butyllithium to 10.6 g (53.5 mmol) of dicyclohexylphosphine dissolved in 30 mL of ether and stirring the mixture for 1 h at 0 °C. After 15 min at -50 °C, the phosphidocuprate was cooled to -75 °C for 15 min, and then 4.83 g (50.3 mmol) of 2-cyclohexen-1-one (Aldrich, distilled and refrigerated) in 20 mL of ether in a septum-sealed 50-mL pear-shaped flask at -75 °C was transferred into it by cannula. After 1 h, a 2.0-mL sample (out of a total of 200 mL) contained 69.0 mg of product (90% yield) measured by calibrated GLC. No starting material was present; therefore, the reaction mixture was quenched with 3 M aqueous ammonium chloride and worked up as described under Method A (above) to give 9.3 g of pale yellow oil, which was distilled by using a short-path stillhead (Firestone design) to obtain three fractions: 1.44 g (40–50 °C/0.2 torr), 4.79 g (56–58 °C/0.2 torr), and 0.42 g (48 °C/0.1 torr). GLC analysis indicated that fractions 2 and 3 were 95% and 97% pure, respectively, but that fraction 1 was ~90% pure. Therefore, it was chromatographed on the Florisil column from method A eluted with 1 L of hexane to remove impurities and then 3 L of 20% ether/hexane to obtain 1.22 g (98% pure by GLC) of product after evaporation under reduced pressure (<30 °C/30 torr). The total yield of 95–98% pure product was 6.43 g (83%): IR (neat) 2935, 2861, 1713, 1450, 1229 cm^{-1}; ^{13}C NMR ($CDCl_3/Me_4Si$) δ 14.0, 22.8, 25.4, 28.9, 31.4, 36.3, 39.1, 41.6, 48.2, 211.7.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.73; H, 11.82.

Acknowledgment. We thank L. Blitzer for Cu and halide analyses.

Registry No. $MeCu(PCy_2)Li$, 88766-01-2; $BuCu(PCy_2)Li$, 83944-05-2; $BuCu(NCy_2)Li$, 83944-04-1; $MeCu(NCy_2)Li$, 88766-02-3; Me_2CuLi, 15681-48-8; $MeCu(PPh_2)Li$, 88766-03-4; $Me_2Cu(CN)Li_2$, 80473-70-7; LiBr, 7550-35-8; $CuBr{\cdot}SMe_2$, 54678-23-8; BuLi, 109-72-8; PCy_2H, 829-84-5; BuCu, 34948-25-9; cyclohex-2-enone, 930-68-7; 1-iodooctane, 629-27-6; cyclohexene oxide, 286-20-4; diethyl cyclopropane-1,1-dicarboxylate, 1559-02-0; 3-methylcyclohexanone, 591-24-2; 3-butylcyclohexanone, 39178-69-3; nonane, 111-84-2; *trans*-2-methylcyclohexanol, 7443-52-9; diethyl propylmalonate, 2163-48-6; diethyl hexylmalonate, 5398-10-7.

Preparation of Dialkyl Carbonates via the Phase-Transfer-Catalyzed Alkylation of Alkali Metal Carbonate and Bicarbonate Salts

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Received September 14, 1983

Esters of carbonic acid are traditionally prepared by the reaction of phosgene with the appropriate alcohol/phenol in the presence of an acid acceptor. Alternatives to the use of phosgene include carbonylation of alcohols[1] and phenols[2] with carbon monoxide and transesterification of ethylene carbonate or certain activated carbonates with alcohols.[3,4]

Recent interest in the utilization of carbon dioxide as a synthetic building block has prompted investigations of the preparation of carbonic esters from CO_2 or its derivatives. For example, the preparation of dialkyl carbonates from CO_2 and alcohols[5] or alkoxides followed by alkylating agents[6] has been reported. Cyclic carbonates have been prepared by the reaction of CO_2 with epoxides[7] or halohydrins[8] in the presence of various catalysts. Although preparation of carbonates from "inorganic" carbonates via alkylation at high temperatures or in dipolar aprotic solvents has been demonstrated,[9] a much more attractive approach is to conduct the alkylation using a phase-transfer catalyst. Thus, the alkylation of potassium carbonate with alkyl bromides can be effected in the presence of organostannyl catalysts.[10] Alkylpolycarbonates have likewise been prepared by alkylation of alkali metal carbonates with difunctional alkyl halides in the presence of crown ethers.[11] A recent report describing the preparation of aliphatic carbonates from potassium bicarbonate and alkyl halides in nonpolar solvents in the presence of phase-transfer catalysts[12] prompts us to disclose the results

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(2) (a) Chalk, A. J. U.S. Pat. 4 096 167, 1978. (b) Hallgren, J. E.; Matthews, R. O. *J. Organomet. Chem*. **1979**, *175*, 135.

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(4) Brunelle, D. J. U.S. Pat. 4 316 981, 1982.

(5) (a) Japan Patent 70 24 966, 1970; *Chem. Abstr*. **1970**, *73* 98378*j*. (b) Yamazaki, N.; Nakahama, S.; Higashi, F. Polymer Preprints, National ACS Meeting, Hawaii.

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(7) (a) Jpn. Pat. 70 38 534, 1971; *Chem. Abstr*. **1971**, *74* 87433*t*. (b) Fr. Pat. 1 543 832, 1968; *Chem. Abstr*. **1970**, *72*, 12085*f*. (c) Japan Patent 76 80 856, 1976; *Chem. Abstr*. **1976**, *85*, 143782*x*. (d) Fumasoni and Pochetti. *Rass. Chim*. **1975**, *27*, 23; *Chem. Abstr*. **1975**, *83*, 113625*q*. (e) Japan Patent 73 68 695, 1973; *Chem. Abstr*. **1974**, *80*, 121538*s*. (f) Japan Patent 72 36 738, 1972; *Chem. Abstr*. **1972**, *77*, 139417*z*. (g) Japan Patent 73 27 314, 1973; *Chem. Abstr*. **1973**, *79*, 136527*r*. (h) Japan Patent 77 35 192, 1977; *Chem. Abstr*. **1977**, *87*, 202345*y*. (i) German Patent 2 611 087, 1976; *Chem. Abstr*. **1977**, *86*, 2979*iv*. (j) Japan Patent 76 141 871, 1976; *Chem. Abstr*. **1977**, *87*, 38863*t*. (k) Japan Patent 77 3064, 1977; *Chem. Abstr*. **1977**, *87*, 38864*u*. (l) Japan Patent 70 38 534, 1970; *Chem. Abstr*. **1971**, *74*, 87433*t*. (m) *Fette Seifen Anstrichen*, **1971**, *73*, 396; *Chem. Abstr*. **1971**, *75*, 129294*b*. (n) Japan Patent 72 1 625, 1972; *Chem. Abstr*. **1972**, *76*, 85406*d*. (o) Japan Patent 72 27 223, 1972; *Chem. Abstr*. **1972**, *77*, 100762.

(8) (a) U.S. Pat. 3 923 842, 1975. (b) Russian Patent, *Chem. Abstr*. **1970**, *73*, 98381*e*.

(9) Hungarian Patent 11 211, 1977; *Chem. Abstr*. **1978**, *88*, 104702*p*.

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