Tetrahedron Vol. 40, No. 9, pp 1457 to 1467, 1984
Printed in Great Britain.

0040 4020/84 $3.00 + .00

HOMOALLYLIC SUBSTITUTION REACTIONS OF LITHIUM DIALKYL CUPRATES WITH CYCLOPROPYLCARBINYL HALIDES: MECHANISTIC CONSIDERATIONS[1a]

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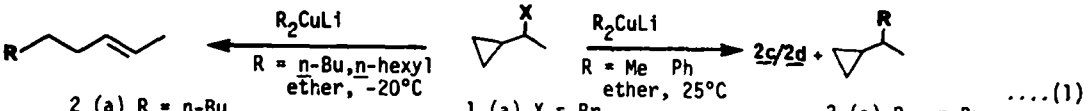
(*Received in USA* 30 *November* 1983)

ABSTRACT: Highly reactive lithium dialkyl cuprates and 1-bromo-1-cyclopropylalkanes, 4, react to give good yields of the homoallylic substitution product, 6. Less reactive organocuprates react with 4 to give mixtures of 6 and the direct substitution product, 7. These results are consistent with a copper(I) radical intermediate which undergoes facile rearrangement prior to reductive coupling.

In contrast to the many studies of cationic ring opening reactions of cyclopropane derivatives,[2] nucleophilic attack on cyclopropane rings under non-cationic conditions has received only cursory attention.[3] The paucity of such studies prompted our recent report in which 1-bromo-1-cyclopropylethane, 1a, was shown to react with lithium dialkyl cuprates to give the homoallylic substitution product, 2,[4] as shown in reaction 1. Posner had previously reported that 1-cyclopropyl-1-ethanol tosylate, 1c, reacted similarly with lithium di-n-butyl cuprate, as in reaction 2, to give E-2-nonene in 49% yield and E-1,3-pentadiene in 23% yield.[5] We observed, however, that 1a



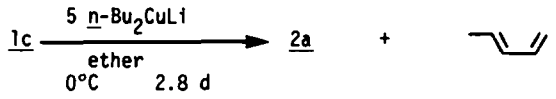
2 (a) R = n-Bu
(b) R = n-hexyl
(c) R = Me
(d) R = Ph

1 (a) X = Br
(b) X = Cl
(c) X = OTs
(d) X = OAc

3 (a) R = n-Bu
(b) R = n-hexyl
(c) R = Me
(d) R = Ph

....(1)

reacted with lithium di-n-butyl cuprate to give only 2-nonene, as a 2:1 mixture of E:Z isomers, in 80% yield. A comparison of the reactivity of 1a and 1c gave the following:[4] (a) reaction of 1a was more facile that reaction of 1c(lower temperatures; shorter reaction time; fewer equivalents of organocuprate); (b) the yield of 2-nonene was higher from 1a; (c) we observed no 1,3-pentadiene or other elimination processes in reaction 1; (d) reaction 1 proceeded with reduced stereoselectivity but the E isomer predominated; (e) we noted little difference in product distribution between the bromide 1a and the chloride 1b, but the latter was much less reactive; (f) reaction of 1a with very reactive organocuprates[lithium di-n-butyl cuprate] gave only 2 but reaction with less reactive organocuprates[lithium dimethyl cuprate] gave mixtures of 2 and 3; (g) the order of reactivity of the organocuprates with 1a or 1b was: t-butyl > n-butyl ~ n-hexyl > phenyl > methyl, the same as that noted for reactions of organocuprates with simple alkyl halides.[6]



.....(2)

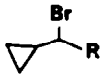
In our initial study we raised questions concerning the mechanistic details of reaction 1. It was not clear if the reaction proceeded via a S_N2' pathway[7] or via the oxidative coupling mechanism proposed by Posner for reaction 2.[5] Posner proposed a copper(II) radical complex or a cuprate(I) cation complex[5a] but found them indistinguishable. Questions have also been raised in the literature concerning the radical nature of organocuprate intermediates. We had initiated a study of the reactivity of organocuprates with a series of highly hindered 1-bromo-1-cyclopropylalkanes, 4, with the goal of establishing the scope of this reaction. The results shed light on the mechanistic questions we had posed prompting this report of our mechanistic explanations as well as experimental details of the reaction of 1a and 4 with organocuprates.

RESULTS

We found that the use of purified copper(I) iodide[8c] or dimethylsulfide-copper(I) bromide[6b] for preparation of the organocuprates gave reduced yields of 2 upon reaction with 1a or 4. We presume this is due to the presence of copper(II) species in the former reagent[6b,c] and electronic variations in the cuprate cluster in the latter.[9] Our best results were obtained by utilizing freshly prepared copper(I) bromide[10] as the precursor to the organocuprate.

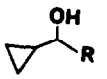
Allylic acetates have been previously shown to be very susceptible to displacement reactions by organocuprates[7] and we prepared 1-cyclopropyl-1-ethanol acetate, 1d, from alcohol 5a. Upon reaction with lithium di-n-butyl cuprate, however, no trace of the homoallylic substitution product, 2, or the direct substitution product, 3, was observed. The products were primarily 5-methyl-5-nonanol[11] and 2-hexanone, resulting from attack at the carbonyl in the acetate moiety. It was therefore clear that cyclopropylcarbinyl acetates were not useful for our study.

We prepared the 1-bromo-1-cyclopropylalkanes 1a and 4a-4c, which we determined should be more reactive that the acetate, based upon our previous study.[4] Treatment of alcohols 5a-5d with triphenylphosphine and bromine, in dimethylformamide, by methods we have recently described,[12] gave the requisite bromides. This new preparative route was ideal for our study since 4 was



4

(a) R = n-Bu
(b) R = iPr
(c) R = t-Bu



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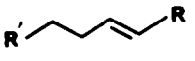
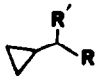
(a) R = Me
(b) R = n-Bu
(c) R = iPr
(d) R = t-Bu



6

	R	R'
(a)	n-Bu	n-Bu
(b)	n-Bu	Me
(c)	iPr	n-Bu
(d)	iPr	Me
(e)	t-Bu	n-Bu
(f)	t-Bu	Me



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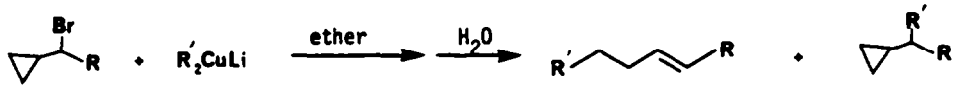
prepared without contamination by the homoallylic bromide or the bromocyclobutane derivatives usually associated with classical preparations of these halides.[12] We chose to study reactions of 4a-4c with lithium di-n-butyl cuprate and lithium dimethyl cuprate since they were representative of the two reaction modes observed with 1a, namely, the former cuprate gave exclusively 2 whereas the latter gave both 2 and 3. We focused exclusively on the bromides since the chlorides were, in every case, less reactive.

Our results are shown in Table 1 and it is noteworthy that the reactivity of 4a-4c was similar to that of 1a for both cuprates, although the reaction was somewhat slower as the steric bulk of 4 increased. Lithium di-n-butyl cuprate reacted with 4 to give 6, exclusively, whereas lithium dimethyl cuprate gave a mixture of 6 and 7 upon reaction with 4. The conversion to substituted products 6 or 7 was comparable to the results obtained in reaction 1 with 1a. As with 1a, we did not observe the presence of the 4-alkyl-1,3-butadiene derivatives observed with 1c and

Table 1. Reaction of 1-Bromo-1-cyclopropylalkanes with Lithium Dialkyl Cuprates.



1/4 2/6 3/7

	R	R'	reaction time(hr)		% 2/6		% 3/7
1a	CH_3	n-Bu	4.5	2a	79[a,c]	3a	-
		CH_3	7.0	2c	42[a,d]	3c	39[d]
4a	n-Bu	n-Bu	6.5	6a	93[b,c]	7a	-
		CH_3	19.5	6b	31[b,d]	7b[e]	42
4b	iPr	n-Bu	7.0	6c	77[b,c]	7c	-
		CH_3	25.0	6d	26[b,d]	7d[e]	51[d]
4c	t-Bu	n-Bu	7.0	6e[e]	75[b,c]	7e	-
		CH_3	19.0	6f	34[b,d]	7f[e]	46[d]

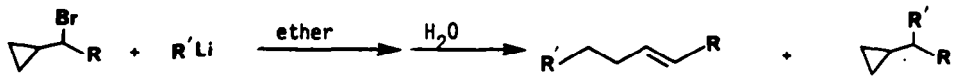
[a] E + Z isomers [b] only E isomer was observed by vpc and vpc/ms [c] isolated yield [d] yield by vpc [e] satisfactory elemental analysis obtained for this compound

elimination does not appear to be a significant process in this reaction.

The yield of 6a,c,e was relatively constant for reaction of 1a and 4 with di-n-butyl cuprate and no 7 was observed. Reaction of 1a and 4 with dimethyl cuprate also gave a relatively constant amount of substitution products, 6b,d,f and 7b,d,f, with the latter predominating. The relative amount of 6 and the ratio of 6:7 was largely independent of the steric impedance around the bromine-bearing carbon in 4 and it appears that the product distribution is primarily dependant upon the structure of the cuprate cluster. The relative amount of 2b, for example, was greater than 6f, although the latter possesses significantly greater steric hindrance. It is clear that 4 reacts almost indentically with 1a in all reactions.

The facility of reaction with 1a and 4 is much greater than the sluggish reactivity reported for secondary halides with organocuprates.[8b,c 13] This enhancement is clearly due to the presence of the cyclopropane ring.[5,14] It was not clear, however, if the reaction of 1a and 4 was similar to the results observed with simple halides. The order of reactivity with organocuprates, as previously mentioned,[4] clearly paralleled that of simple halides.[6] Uncatalyzed reactions of alkyllithium reagents with alkyl halides are usually characterized by low yields of coupling products and a multitude of products resulting from side reactions.[15] This is in contrast to the facile and clean results observed with organocuprates. It appears that this reaction proceeds, in part, through a complex free-radical mechanism.[16] We examined the reactivity of 1a and 4 with n-butyllithium and methyllithium as a comparison with similar reactions with simple alkyl halides. We primarily wished to observe the product distribution which would arise from 1a or 4 via a 'free' radical mechanism. Phenyllithium was used in the case of 1a since methyllithium produced volatile products. These results are shown in Table 2 and indicate that alkyllithium reagents react with 4 to give 6 and 7, but in very poor yield. In addition, a number of unidentified but clearly not substitution products accompanied these reactions and this approach is generally inferior for substitution of 4 when compared to the organocuprates. This is precisely what is observed with simple alkyl halides. One concludes that, except for enhanced reactivity, 4 behaves similarly to other alkyl halides. It is not, therefore, necessary to invoke exotic pathways peculiar to the cyclopropylcarbinyl system. It is also apparent that the product distribution from 4 is not consistent with a 'free' radical intermediate, although a metal-bound radical or a 'tight radical pair' are not ruled out.

Table 2. Reaction of 1-Bromo-1-cyclopropylalkanes with Alkyllithium Reagents.



1/4 2/6 3/7

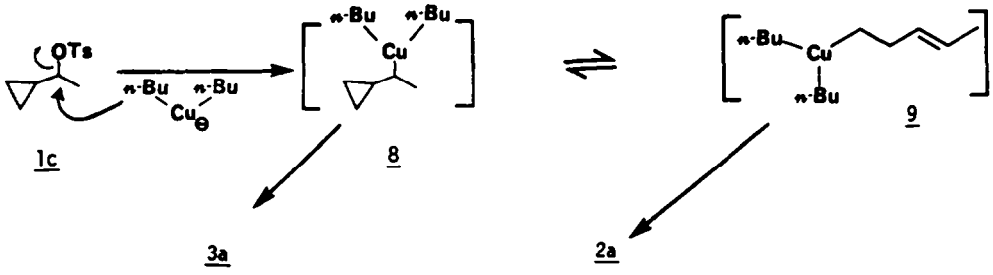
	R	R'		% 2/6[a,b]		% 3/7[b]
1a	CH_3	n-Bu	2a	5		-
4a	n-Bu		6a	9	7a	18
4b	iPr		6c	15		-
4c	t-Bu		6e	18		-
4a	n-Bu	CH_3	6b	3	7b	9
4b	iPr		6d	5	7d	5
4c	t-Bu		6f	5	7f	3
1a	CH_3	Ph		-	7g	40

[a] yield via vpc [b] E + Z isomers

DISCUSSION

Posner has suggested an oxidative addition mechanism[5,6,8] for reaction 2 via a S_N2-like displacement[5] to give a copper(III) species, 8, as shown in Scheme I. This is the widely accepted mechanism for reaction of organocuprates with alkyl halides[5,6,8] and reductive elimination of 8 gave 3a. Reaction of 1c did not give 3a, however, but rather 2a, suggesting a rapid rearrangement of 8 to 9.[5] Posner suggested that 8/9 was a copper(II) radical complex or a cuprate(I) cation complex.[5a] Formation of only rearranged product, 2a, in an irreversible process from 1c argued against a cation intermediate[5a] but stereospecific formation of E-2a supported the intermediacy of cations[5a] by analogy with Julia's results.[17] These pathways were proposed by Posner but were indistinguishable and both must be considered for the reaction shown in Table 1.

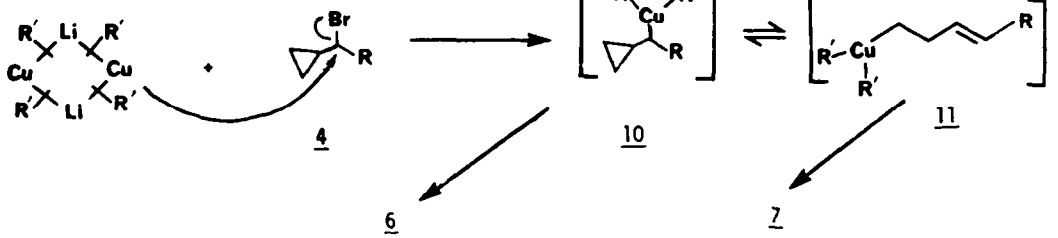
SCHEME I[5]



One could envision direct displacement of bromide from 1a or even 4a, as in Scheme II, directly analogous to Posner's observations. The severe steric hindrance in 4c clearly precludes such a pathway, however, and forces a reconsideration of the process which generates 10 or 11. The neopentyl nature of 4c suggested one alternative. Posner has studied the reaction of neopentylic tosylates with organocuprates[18] and found that substitution, elimination and reduction occurred. The mechanism for the process was not determined but Posner suggested the lithium cuprate assisted loss of the tosylate group by acting as a Lewis acid.[5a] This clearly suggested a cationic pathway and skeletal rearrangements were observed, reminescent of cationic rearrangements. Although 4c may react analogously with neopentyl tosylates, this would not explain the similarity in reaction products for 1a and 4c. In addition, we did not observe elimination products in any reaction with 4 and we discount this as a dominant process.

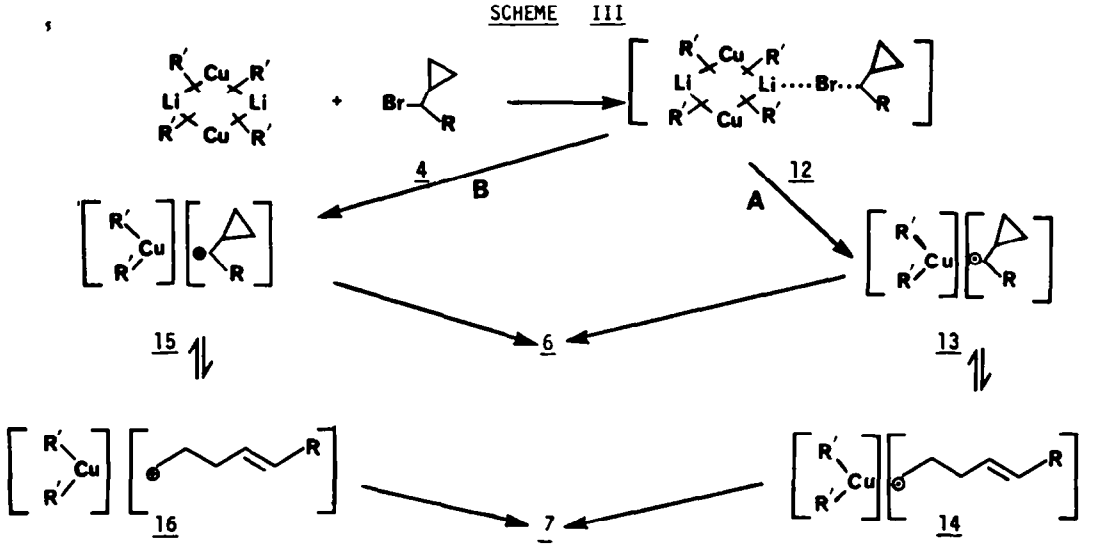
In Scheme II, Posner's intermediate 10 has been shown as the radical, 13, and also the cation 15, to reflect the ambiguity suggested by Posner. Since it is clear that rearrangement of the

SCHEME II



cyclopropylcarbinyl system had occurred, completely upon reaction with di-n-butyl cuprate and partially with dimethyl cuprate, we have also shown the homoallylic systems 14 and 15. In addition, we have assumed ionization of halide 4, assisted by the cyclopropane ring and lithium in the cuprate cluster, as shown in 12, to be responsible for formation of 13 or 15, rather than the oxidative addition of Scheme I. This assumption is based on the observed insensitivity to steric hindrance in 4 for reaction with organocuprates, a condition contrary to a S_N2-like displacement. Reaction of cuprates with enones via a transient charge transfer complex between oxygen and the cuprate[19] and a related association of cuprate and bromide known for aryl halides[20] gave credence to the assumed formation of 12. Similar arguments are reported by Johnson[8d] for radical intermediates derived from simple alkyl halides and organocuprates.

SCHEME III



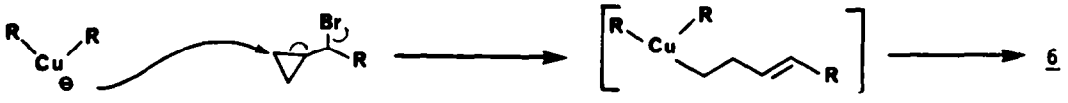
Either path A(cationic) or path B(radical) allow rearrangement to 14 or 16, respectively, and conversion to the observed products 6 and 7. It has been shown that such rearrangement occurs during and not prior to reaction with the organocuprate.[5] Path A suggests an intermediate cyclopropylcarbinyl cation, 15, analogous to that suggested by House.[6b] Reversible but facile rearrangement to 16 would account for the observed products. Path B suggests a one-electron transfer from 12 to give a cyclopropylcarbinyl radical intermediate, 13. Rearrangement to 14 also leads to 6. Johnson has suggested that if an alkyl radical is an intermediate, loss of configurational identity is likely if the free radical has any lifetime. Existence of the free radical species as a 'tight' radical anion pair, rapidly attacked by the copper(II) species formed, could lead to inversion of configuration, although, as Johnson suggests, not with complete stereospecificity.[8d] Ashby has recently shown evidence for inversion of configuration in reactions involving radical processes,[21] the result of formation of a radical anion pair in a solvent cage. Backside attack

$$Me_3Sn^- + RX \longrightarrow [Me_3Sn^{\cdot}, RX^-] \longrightarrow [Me_3Sn^-, R^{\cdot}, X^-] \longrightarrow Me_3SnR + X^- \quad \ldots\ldots (3)$$

occurs while the front side is still protected by the leaving group, as in reaction 3. In addition, Huyser has shown[22b] that cyclopropylcarbinyl radicals open to give exclusively the E isomer, analogous to Julia and Johnson's results for cyclopropylcarbinyl cations.[17] It has also been shown by several groups[22] that the 'free' cyclopropylcarbinyl radical rearranges quantitatively with a rate of 10^8 sec^{-1}, to the homoallylic radical.[22a] The regiochemistry of 6 is therefore consistent with 13/14 as an intermediate.[5] Ashby has also shown that single electron transfer occurs in reaction of organocuprates with alkyl halides,[23] and he suggested a radical pair, analogous to 13/14 for reaction of alkyl iodides with lithium dimethyl cuprate. The corresponding bromide, however, is thought to react predominantly, but not exclusively, via a S_N2 pathway.[23] The enhanced reactivity induced by the cyclopropane ring as well as the special stability of cyclopropylcarbinyl radicals could account for the behavior observed for 1 and 4.

Another direct substitution mechanism must be considered which is consistent with the observed results. As shown in Scheme IV, a S_N2'-like displacement on the cyclopropane ring of 4, by cuprate, would generate 14/16, directly, and thereby, 6. This mode of reaction must be a

SCHEME IV



14/16

function of the steric environment at the bromine-bearing carbon, however, as with S_N2' reactions observed in allylic systems.[7] This would be favorable for 4c and, perhaps, 4b, but a S_N2-type displacement would dominate reactions with 1a and 4a. A S_N2' pathway, therefore, does not account for the presence of 7 as the major product upon reaction with 1 and 4 and dimethyl cuprate; nor, for the lack of 7 from reaction of 1a and 4a with lithium di-n-butyl cuprate.

A radical precursor appears to explain the results we have just discussed. Path B, in Scheme III, would lead to 13, the copper-bound cyclopropylcarbinyl radical. If radical 13 is bound tightly to copper, little rearrangement would be expected and a mixture of 6 and 7 should result. If 13 is loosely bound, however, the facility of the homoallylic rearrangement would lead to extensive rearrangement to 14 and little or no 7 would be observed. It is noted that formation of 12 as an intermediate would render elimination reactions difficult, consistent with the observed results.

It has been shown that the size and geometry of the cuprate cluster may vary from the dimeric, classical representation in Schemes II and III(postulated for lithium dimethyl cuprate)[24] with different alkyl groups.[6b] Electronic changes in the cluster, provided by coordinating solvents, also affect the reactivity.[9] It is therefore reasonable that when di-n-butyl cuprate is compared with dimethyl cuprate, the increased steric hindrance and change in the aggregation state, in the cuprate cluster, may lead to differences in the binding of the radical in 13. This would suggest independence of the steric environment of the halides, as was observed. The increased stereoselectivity for 4, compared to 1, appears to be independent of the phenomena just described. Rearrangement occurs when 13 is 'released' and the increased amount of the E isomer is probably due to the increased thermodynamic stability of this isomer[17,22b] and is not greatly influenced by the cuprate cluster. It is clear, however, that the 'release' of the radical does not involve a 'free' radical, analogous to those produced in reactions of alkyl halides with alkyllithium reagents since the results shown in Tables 1 and 2 are strikingly different.

Similar arguments could be made for binding cationic complex 15 to the cuprate cluster and rearrangement to 16. If one assumes a cationic complex, however, dialkyl cuprates must be electrophilic enough to promote cationic ionization in 12. Contrary to previous statements,[5a] Cristol clearly states that syn- or anti-7-chlorobenzonorbornadiene, very susceptible to cationic rearrangements upon reaction with Grignard reagents, does not undergo reaction with lithium dialkyl cuprates.[25] Cristol interprets this to mean that the reagent is "not electrophilic enough to

promote ionization of the halide."[25] One must, therefore, question path A. In addition, the cyclopropylcarbinyl cation has been studied extensively [26] and usually leads to a mixture of products analogous to 6 and 7, but, significant amounts of cyclobutane derivatives are observed also.[26] Clearly, binding the cation to the cuprate cluster could alter this reactivity but the lack of any cyclobutane derivatives and the obvious parallels with radical chemistry suggest path B as the most likely mechanistic rationale.

Another explanation of these results could invoke a S_N2 or S_N2' type mechanism for di-n-butyl cuprate, as in Schemes II and IV, and a radical type intermediate for dimethyl cuprate, as in Scheme III. If Scheme IV dominates the reactions of di-n-butyl cuprate, one must explain the insensitivity to steric hindrance since direct substitution of 1a or 4a to 6 was not observed. Exclusive S_N2'-like attack would explain the results and it is possible that the increased 'size' of the cuprate cluster could induce this pathway but the results of Posner in reaction 2 and our own do not give credence to this idea. Although tosylates and halides are known to react with organocuprates via different mechanisms, there appears to be no evidence to suggest duality of mechanism with 4. It is also possible that both mechanisms are operative and in competition but the virtual identity of reactivity of 1a and 4c militate against this explanation, although it cannot be completely excluded.

It is clear that 1-bromo-1-cyclopropylalkanes are more reactive than tosylate 1c upon reaction with lithium organocuprates. This is consistent with the reduced reactivity of secondary tosylates compared to secondary bromides.[8d] Reactions with reactive organocuprates, such as di-n-butyl cuprate, leads exclusively to the homoallylic substitution product with high regioselectively for the E isomer, independent of the steric impedance at the bromine-bearing carbon. Reaction with relatively unreactive organocuprates such as dimethyl cuprate leads to a mixture of homoallylic and direct substitution products, with the latter predominating, once again independent of the steric environment of the halide. These results appear to preclude a direct substitution(S_N2) type displacement of the cuprate and point to a copper mediated cyclopropylcarbinyl radical which undergoes facile rearrangement to the homoallylic radical, as the key intermediate. Reductive elimination leads to the observed products in accord with previous results with simple alkyl halides. The synthetic value of the reaction is confined to reaction of cyclopropylcarbinyl halides with reactive organocuprates to give the E alkene, in high yield.

EXPERIMENTAL

All ^1H nmr were recorded at 60 MHz on a Varian Associates EM-360 instrument, in ppm, downfield from tetramethylsilane. The mass spectra were recorded on an A.E.I. MS-9 mass spectrometer at 70 eV or on a HP 5987 gc/ms instrument utilizing a 30 meter, SE-54 capillary column. Infra-red spectra were recorded on a Perkin-Elmer IR-283 instrument. The qualitative and quantitative vpc work was accomplished on a Perkin-Elmer 3920-B gas chromatograph using a 5.9 meter, 20% SE-30 Chromosorb W column. Elemental analyses were performed by MicAnal, Tucson, Arizona, USA.

The n-butyllithium(2.0 M in n-hexane), methyllithium(1.22 M in ether) and phenyllithium(1.0 M in cyclohexane/ether) were obtained from Alfa and standardized prior to use with diphenylacetic acid.[27] The copper(I) bromide used to prepare the organocuprates was prepared by the method of Corey and Kende.[10] The 1-cyclopropyl-1-ethanol, undecane, decane, n-hentane and toluene were obtained from Aldrich. The Z-2-nonene, E-2-nonene and E-2-hexene were obtained from FMI Chemicals. The ether was distilled prior to use(under Ar) from sodium/benzophenone. The requisite bromides, 4a-4c and 1a were obtained from the corresponding alcohol, 5a-5d, via treatment with bromine and triphenylphosphine in DMF at -10°C.[12] In this manner, 1-cyclopropyl-1-ethanol was converted to 1a; 1-cyclopropyl-1-pentanol[12b,28] to 4a; 1-cyclopropyl-2-methyl-1-propanol[12b,29] to 4b; and, 1-cyclopropyl-2,2-dimethyl-1-propanol[12b,30] to 4c.

General Procedure for Reaction of 1-Bromo-1-cyclopropylalkanes with Lithium Dialkyl Cuprates:

A slurry of freshly prepared copper(I) bromide in 20 mL of ether was cooled to -78°C (acetone/CO_2) and treated with the appropriate alkyllithium. The solution was warmed to -42°C (acetonitrile/CO_2) and stirred for 10 min. A solution of the bromide(1a, 4a-4c) in 2 mL of ether was added at -42°C. The solution was then stored at -24°C(for n-butyl) or 25°C(for methyl) for

the indicated time, quenched with 4 mL of water and the mixture filtered through a Celite pad. The black solids were washed with 0.15 L of ether, in portions, and the filtrate was dried($MgSO_4$) prior to removal of solvents by distillation through a 15 cm Vigreux column. The resulting oil was analyzed by ^1H nmr and vpc as well as by vpc/ms. Isolation was accomplished via preparative vpc utilizing a SE-30/Chromosorb W column. The yields were obtained by analysis on vpc utilizing the indicated internal standards. The analytical samples were isolated by preparative vpc.

Reaction of Lithium di-n-butyl Cuprate:

(a) with 1-Cyclopropyl-1-ethanol Acetate, 1d: Treatment of the organocuprate formed from 0.48 g (3.36 mmol) of CuBr and 2.8 mL of 2.4 M n-BuLi with 0.215 g (1.68 mmol) of 1d gave, after 15.5 h, a colorless oil. Analysis by vpc and ^1H nmr indicated the presence of 5-methyl-5-nonanol:[11] ^1H nmr($CDCl_3$) δ 0.90(6H, dist. t), 11.08(s, 3H), 1.15-1.55(12H, bd. m) and 2.26 ppm(1H, s, OH); and, 2-hexanone:[31] ^1H nmr ($CDCl_3$): δ 0.90(3H, dist. t), 1.1-1.72(4H, m), 2.07(s, 3H) and 2.36 ppm(2H,t).

(b) with 1-Bromo-1-cyclopropylethane, 1a: Treatment of the organocuprate formed from 0.48 g (3.36 mmol) of CuBr and 3.35 mL of 2.0 M n-BuLi with 0.25 g (1.68 mmol) of 1a gave, after 4.5 h, a colorless oil which contained 2-nonene, 2a: ^1H nmr($CDCl_3$) δ 0.90(dist. t, 3H), 1.15-1.60(m, 8H), 1.59(d, 3H), 1.70-2.1(m, 2H) and 5.23-5.68 ppm(m, 2H, CH=CH); mass spectrum, m/z(rel. intensity): 126(45, $M^{+\cdot}$), 55(100, $M^{+\cdot}-C_5H_{11}$), 56(45, $M^{+\cdot}-C_5H_{10}$) and 97(20), 84(18), 83(18), 70(40), 69(37), 43(25) and 41(30).

Analysis by vpc with undecane as an internal standard indicated 0.17 g (1.35 mmol) of 2a(80%). Comparison with authentic E-2-nonene and Z-2-nonene indicated a 2:1 mixture of E:Z 2a.

(c) with 1-Bromo-1-cyclopropylpentane, 4a: Treatment of the organocuprate formed from 0.375 g (2.63 mmol) of CuBr and 3.8 mL of 1.4 M n-BuLi with 0.25 g (1.31 mmol) of 4a gave, after 6.5 h, a colorless oil which contained E-5-dodecene, 6a:[32] ^1H nmr($CDCl_3$): δ 0.90(dist. t, 6H), 1.05-1.71 (m, 14 H), 1.5-2.2(m, 4H) and 5.35-5.65 ppm(m, 2H, CH=CH); mass spectrum, m/z(rel. intensity: 168 (25, $M^{+\cdot}$), 55(100, $C_4H_7^{+\cdot}$), 97(25, $M^{+\cdot}-C_5H_{11}$) and 98(12), 84(25), 83(45), 70(53), 69(73), 57(25), 56(53), 43(30) and 41(50).

Analysis by vpc with decane as an internal standard indicated 0.205 g (1.22 mmol) of 6a(93%).

(d) with 1-Bromo-1-cyclopropyl-2-methylpropane, 4b: Treatment of the organocuprate formed from 0.405 g (2.84 mmol) of CuBr and 4.1 mL of 1.4 M n-BuLi with 0.25 g (1.41 mmol) of 4b gave, after 7 h, a colorless oil which contained E-2-methyl-3-decene, 6c:[33] ^1H nmr($CDCl_3$) δ 0.88(dist. t, 3H), 0.98(d, 6H, J = 3.5 Hz), 1.1-1.68(m, 10H), 1.8-2.2(m, 2H), 2.3-2.9(m, 1H) and 5.25-5.65 ppm(m, 2H, CH=CH); mass spectrum, m/z(rel. intensity): 154(23, $M^{+\cdot}$), 69(100, $C_5H_9^{+\cdot}$), 83(25, $M^{+\cdot}-C_5H_{11}$), 139 ($M^{+\cdot}-CH_3$), 98(8, $M^{+\cdot}-C_4H_8$) and 97(10), 84(12), 70(27), 57(22), 56(55), 43(10) and 41(20).

Analysis by vpc with E-2-nonene as an internal standard indicated 0.167 g (1.08 mmol) of 6c (77%).

(e) with 1-Bromo-1-cyclopropyl-2,2-dimethylpropane, 4c: Treatment of the organocuprate formed from 0.376 g (2.63 mmol) of CuBr and 3.9 mL of 1.4 M n-BuLi with 0.25 g (1.31 mmol) of 4c gave, after 7 h, a colorless oil which contained E-2,2-dimethyl-3-decene, 6e: ^1H nmr($CDCl_3$): δ 0.89(dist. t, 3H), 1.00(s, 9H), 1.1-1.65(m, 4H), 1.75-2.2(m, 2H) and 5.25-5.55 ppm(m, 2H, CH=CH); mass spectrum, m/z(rel. intensity): 168(15, $M^{+\cdot}$), 83(100, $C_6H_{11}^{+\cdot}$), 97(27, $M^{+\cdot}-C_5H_{11}$), 153(18, $M^{+\cdot}-CH_3$) and 84(25), 70(20), 69(70), 55(33) and 41(25). $C_{12}H_{24}$ requires: m/z, 168.1879. Found: m/z, 168.1870.

Analysis by vpc with Z-2-nonene as an internal standard indicated 0.165 g (0.98 mmol) of 6e (75%).

Reaction of Lithium Dimethyl Cuprate:

(a) with 1a: Treatment of the organocuprate formed from 0.48 g (3.36 mmol) of CuBr and 5.5 mL of 1.22 M methyllithium with 0.25 g (1.18 mmol) of 1a gave, after 7 h, a colorless oil which contained: 2-hexene, 2c: ^1H nmr($CDCl_3$): δ 0.90(t, 3H), 1.1-1.6(m, 2H), 1.6(d, 3H), 1.7-2.2(m, 2H) and 5.05-5.30 ppm(m, 2H, CH=CH); mass spectrum, m/z(rel. intensity): 84(75, $M^{+\cdot}$), 69(34, $M^{+\cdot}-CH_3$), 55(100, $M^{+\cdot}-C_2H_5$), 56(30, $M^{+\cdot}-C_2H_4$) and 42(30) and 41(30); and, 2-cyclopropylpropane, 3c:[38] ^1H nmr($CDCl_3$): δ 0.03-0.80(m, C_3H_5) and 1.78 ppm(d, 6H); mass spectrum, m/z(rel. intensity): 84(5, $M^{+\cdot}$), 69(20, $M^{+\cdot}-CH_3$), 56(100, $M^{+\cdot}-C_2H_4$) and 55(15), 43(12) and 41(43).

Analysis by vpc with n-heptane as an internal standard indicated 0.061 g (0.72 mmol) of 2c (43%) as a 5:1 mixture of E:Z 2c, by comparison with authentic E-2-hexene, as well as 0.054 g (0.64 mmol) of 3c(38%).

(b) with 4a: Treatment of the organocuprate formed from 0.375 g (2.63 mmol) of CuBr and 4.0 mL of 1.22 M methyllithium and 0.25 g (1.31 mmol) of 4a gave, after 19.5 h, a colorless oil which contained: E-4-nonene, 6b:[34] ^{1}H nmr($CDCl_3$): δ 0.91(dist. t, 6H), 1.1-1.65(m, 6H), 1.7-2.2(m, 4H) and 5.30-5.80 ppm(m, 2H, CH=CH); mass spectrum, m/z(rel. intensity): 126(36, $M^{+\cdot}$), 55(100, $C_4H_7^{+\cdot}$), 83(20, $M^{+\cdot}-C_3H_7$), 84(15, $M^{+\cdot}-C_3H_6$), 97(18), $M^{+\cdot}-C_2H_5$) and 70(35), 69(33), 56(40), 43(12) and 41(42); and, 2-cyclopropylhexane, 7b: ^{1}H nmr($CDCl_3$): δ 0.03-0.08(m, 4H, C_3H_4), 0.89(dist. t, 3H), 0.93(d, 3H, J = 3.0 Hz), 0.9-1.2(m, 7H) and 1.4-1.9 ppm(m, 1H); mass spectrum, m/z(rel. intensity): 126(1, $M^{+\cdot}$), 56(100, $C_4H_8^{+\cdot}$), 69(62, $M^{+\cdot}-C_4H_9$) and 98(24), 85(10), 84(20), 83(15), 70(48), 57(20), 55(47), 43(30) and 31(64); C_9H_{18} requires C, 85.63; H, 14.37. Found: C, 85.94; H, 14.62.

Analysis by vpc with undecane as an internal standard indicated 0.051 g (0.40 mmol) of 6b (31%) and 0.062 g (0.49 mmol) of 7b(37%).

(c) with 4b: Treatment of the organocuprate formed from 0.405 g (2.84 mmol) of CuBr and 4.4 mL of 1.22 M methyllithium with 0.25 g (1.41 mmol) of 4b gave, after 25 h, a colorless oil which contained: E-2-methyl-3-heptene, 6d:[35] ^{1}H nmr($CDCl_3$): δ 0.89(dist. t, 3H), 0.98(d, 6H, J = 3.5 Hz), 1.1-1.65(m, 4H), 1.75-2.45(m, 3H) and 5.31-5.58 ppm(m, 2H, CH=CH); mass spectrum, m/z(rel. intensity): 112(1, $M^{+\cdot}$), 69(100, $C_5H_9^{+\cdot}$), 83(12, $M^{+\cdot}-C_2H_5$), 97(5, $M^{+\cdot}-CH_3$) and 84(37), 70(15), 55(20), 43(10) and 41(27); and, 2-cyclopropyl-3-methylbutane, 7d: ^{1}H nmr($CDCl_3$): δ 0.05-0.68(m, 4H, C_3H_4), 0.90(d, 6H, J = 3.5 Hz), 0.94(d, 2H, J = 3.0 Hz), 0.9-1.8(m, 2H), 1.2-1.50(m, 1H) and 1.4-1.9 ppm (m, 1H); mass spectrum, m/z(rel. intensity): 112(52, $M^{+\cdot}$), 69(100, $M^{+\cdot}-C_3H_7$), 97(20, $M^{+\cdot}-CH_3$) and 96(50), 81(94), 79(50), 56(33), 55(58) and 41(30); C_8H_{16} requires C, 85.63; H, 14.37. Found: C, 86.00; H, 14.30

Analysis by vpc with E-2-nonene as an internal standard indicated 0.04 g (0.36 mmol) of 6d (26%) and 0.081 g (0.72 mmol) of 7d(51%).

(d) with 4c: Treatment of the organocuprate formed from 0.376 g (2.63 mmol) of CuBr and 4.1 mL of 1.22 M methyllithium with 0.25 g (1.31 mmol) of 4c gave, after 19 h, a colorless oil which contained: E-2,2-dimethyl-3-heptene, 6f:[36] ^{1}H nmr($CDCl_3$): δ 0.88(t, 3H, J = 3.5 Hz), 0.99(s, 9H), 1.2-1.6(m, 2H), 1.7-2.2(m, 2H) and 5.25-5.52 ppm(m, 2H, CH=CH); mass spectrum, m/z(rel. intensity): 126(1, $M^{+\cdot}$), 69(100, $C_5H_9^{+\cdot}$), 98(15, $M^{+\cdot}-C_2H_4$), 111(4, $M^{+\cdot}-CH_3$) and 83(28), 70(30), 57(45), 55(25) and 41(37); and, 2-cyclopropyl-3,3-dimethylbutane, 7f: ^{1}H nmr($CDCl_3$): δ 0.15-0.65(m, 4H, C_3H_4), 0.88(s, 9H), 0.94(d, 3H, J = 3.0 Hz) and 1.4-1.9 ppm(m, 1H); mass spectrum, m/z(rel. intensity): 126(20, $M^{+\cdot}$), 69(100, $C_5H_9^{+\cdot}$), 83(75, $M^{+\cdot}-C_3H_7$), 111(12, $M^{+\cdot}-CH_3$) and 97(10), 84(20), 55(39) and 41(23); C_9H_{18} requires C, 85.63; H, 14.37. Found: C, 86.00; H, 14.52.

Analysis by vpc with Z-2-nonene as an internal standard indicated 0.056 g (0.44 mmol) of 6f (34%) and 0.076 g (0.60 mmol) of 7f(46%).

General Procedure for Reaction of 1a and 4a-4c with Alkyllithium Reagents:

A solution of the halide, in 25 mL of ether(chilled to -78°C) was treated with the appropriate alkyllithium reagent and allowed to warm to -20°C(n-BuLi) or 25°C(methyllithium and phenyllithium) and then stirred for 20 h(n-BuLi) or 25 h(methyllithium or phenyllithium). The reaction was quenched with 2 mL of water, the organic phase separated and dried($MgSO_4$) and the solvents were removed by distillation through a 15 cm Vigreux column. An internal standard was added to the resulting colorless oil and the mixture was analyzed by vpc and vpc/ms to determine the yield and identify the products, which had been previously identified with the organocuprate reactions.

Reaction of n-Butyllithium:

(a) with 1a: A yield of 0.011 g (0.08 mmol) of 2-nonene, 2a(5%), was obtained from 0.25 g (1.68 mmol) of 1a and 2.1 mL of 1.6 M n-BuLi with undecane as the internal standard.

(b) with 4a: A yield of 0.022 g (0.12 mmol) of 6a(9%) and 0.04 g (0.024 mmol) of 7a(18%) was obtained from 0.25 g (1.31 mmol) of 4a and 1.64 mL of 1.6 M n-BuLi with decane as an internal standard.

(c) with 4b: A yield of 0.033 g (0.21 mmol) of 6c(15%) was obtained from 0.25 g (1.41 mmol) of 4b and 1.76 mL of 1.6 M n-BuLi with Z-2-nonene as an internal standard.

(d) with 4c: A yield of 0.040 g (0.24 mmol) of 6e(18%) was obtained from 0.25 g (1.31 mmol) of 4c and 1.64 mL of 1.6 M n-BuLi with Z-2-nonene as an internal standard.

Reaction of Methyllithium:

(a) with 4a: A yield of 0.005 g (0.04 mmol) of 6b(3%) and 0.015 g (0.012 mmol) of 7b 9%) was obtained from 0.25 g (1.31 mmol) of 4a and 2.0 mL of 1.3 M methyllithium with undecane as an internal standard.

(b) with 4b: A yield of 0.008 g (0.07 mmol) of 6d(5%) and 0.008 g (0.07 mmol) of 7d(5%) was obtained from 0.25 g (1.41 mmol) of 4b and 2.17 mL of 1.3 M methyllithium with E-2-nonene as an internal standard.

(c) with 4c: A yield of 0.008 g (0.07 mmol) of 6f(5%) and 0.005 g (0.04 mmol) of 7f(3%) was obtained from 0.25 g (1.31 mmol) of 4c and 2.0 mL of 1.3 M methyllithium with undecane as an internal standard.

Reaction of Phenyllithium:

(a) with 1a: A yield of 0.099 g (0.68 mmol) of 5-phenyl-2-pentene,[37] 7g(40%), was obtained from 0.25 g (1.69 mmol) of 1a and 1.93 mL of 1.74 M phenyllithium with toluene as an internal standard.

ACKNOWLEDGEMENTS

We thank the Leo H. Baekeland Fund of the Research Corporation for funding of this work. We thank Mr. Gary Lavigne who performed the vpc/ms analyses, and Mr. Marvin Thompson who performed the remaining mass spectral analyses.

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