Mechanism of Organocalcium Reagent Formation[1]

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The stereochemistry of the reaction of (*S*)-(+)-1-bromo- and (*S*)-(+)-1-chloro-1-methyl-2,2-diphenylcyclopropane and (*S*)-(+)-1-bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane with calcium–aromatic complexes is reported as is its reaction with a radical clock, 6-chloro-6-methyl-1-heptene. Evidence is presented which indicates that these reactions occur by a single electron transfer to yield free radicals as intermediates. The reduction of a number of these substrates with solutions of calcium dissolved in liquid ammonia is also reported. Metallic bronze $Ca(NH_3)_6$ in THF at −30 °C behaves as a solid surface in its reaction with alkyl halides.

Introduction

Of the available methods for reduction of organic halides with dissolving metals, the most popular have been the uses of solutions of alkali metal naphthalenides[2,3] and dissolved metals in liquid ammonia.[4-6] Several mechanistic studies have described the kinetics and stereochemistry of such reductions.[7-9] However, attention was mainly focused on carbon–halogen bond breaking effected by alkali metal naphthalenides and dissolved sodium in ammonia.[10]

Recently Rieke[11] reported that "highly reactive calcium" obtained by reduction of calcium halides with preformed lithium biphenylide in THF was capable of reacting with primary, secondary, and tertiary alkyl halides to form organocalcium reagents which underwent Grignard-type reactions. The significance of this work is that it provided a convenient means, which had been lacking, for preparing organocalcium compounds.[12] The questions that arise are the following: (a) Does the formation of organocalcium reagents under such conditions occur via halogen–metal exchange or electron transfer? (b) Are radicals and/or radical anions formed as intermediates? (c) What is the stereochemistry of this reaction? (d) What is the most likely structure of the calcium–aromatic complex?

We now hope to shed some light on these questions by our investigation of the mechanism of formation of organocalcium reagents by the direct reaction of organic halides with calcium–aromatic complexes such as calcium–biphenyl and calcium–naphthalene. Additionally we have investigated the mechanism of the carbon–halogen bond cleavage effected both by the blue dilute solutions of calcium dissolved in liquid ammonia (solvated electron–calcium cation pair)[5] and the concentrated solutions which gives rise to a solid bronze $Ca(NH_3)_6$ complex.[5]

The first substrates selected for this investigation were the cyclopropyl systems. These provide a distinct advantage since, in contrast to other saturated hydrocarbons, the organometallic reagents prepared from them such as lithium, magnesium, zinc, and mercury compounds are known to be configurationally stable. Another feature is that the cyclopropyl radical is a σ radical which inverts its configuration at a rate of 10^{11} s^{-1}.

The cyclopropyl molecules selected for this study were (*S*)-(+)-1-bromo-1-methyl-2,2-diphenylcyclopropane (**1**),[13] (*S*)-(+)-1-chloro-1-methyl-2,2-diphenylcyclopropane (**2**),[13] and (*S*)-(+)-1-bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane (**3**),[14] all of which have been prepared previously and whose absolute configurations and optical purities are known as are those of their derivatives (*R*)-(−)-1-methyl-2,2-diphenylcyclopropane (**5**) and (*S*)-(−)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid (**6**).

Another system of interest was 6-chloro-6-methyl-1-heptene (**4**), a radical clock for which kinetic data have been firmly established.[15,16] The synthesis of 6-chloro-

(1) This work was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society and in part from the National Science Foundation to whom we are grateful.

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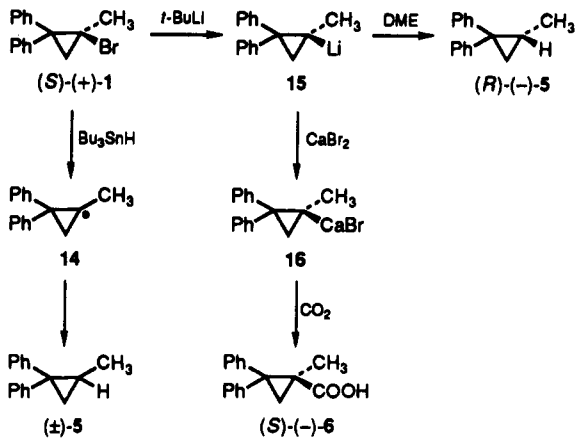
Scheme I



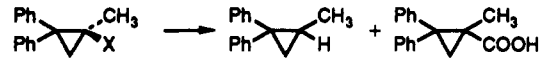
6-methyl-1-heptene (4)[15] was achieved starting with 5-hexenoic acid according to the method described by Ashby and Oswald.[15a] Authentic samples of the products expected from the reduction of 4, 1,1,2-trimethylcyclopentane (12), 6-methyl-1-heptane (11), and 2-methyl-1,6-heptadiene (13) have been prepared previously.[16]

Optically Pure Cyclopropylcalcium Bromide

In the course of several earlier investigations involving cyclopropyl radicals, it had been established[17] that when the 1-methyl-2,2-diphenylcyclopropyl radical (14) was generated *in solution* from optically active precursors, either by decomposition of diacyl peroxide or by reaction of the bromide 1 with tri-*n*-butyltin hydride, the resulting hydrocarbon 5 was completely racemic, thus demonstrating that the radical was incapable of maintaining its configuration under homogeneous conditions (Scheme I).

By contrast the halogen–lithium exchange of optically pure bromide 1 with butyllithium was shown to occur with complete retention of optical activity and configuration.[13] The (1-methyl-2,2-diphenylcyclopropyl)lithium (15) formed was stable at room temperature in ether. However, 15 was rapidly quenched to give 5 by addition of 1,2-dimethoxyethane. In order to establish the configurational stability of cyclopropylcalcium 16 optically pure (1-methyl-2,2-diphenylcyclopropyl)lithium (15) was formed by halogen–lithium exchange of 1 with *tert*-butyllithium in ether and treated with anhydrous calcium bromide. An excess of 1,2-dimethoxyethane was added in order to decompose any 15 that might still be present and this was followed by carbonation of the reaction mixture giving rise to 69% of 1-methyl-2,2-diphenylcyclopropane (5) and 25% of 1-methyl-2,2-diphenylcyclopropanecarboxylic acid (6), both with complete retention of optical activity and configuration. That 6 was obtained in optically pure form demonstrates that once the cyclopropylcalcium bond is formed it is capable of maintaining its optical activity and configuration. This method was previously used to prepare and establish the stability of an optically pure Grignard reagent.[18]

Table I. Reduction of (*S*)-(+)-1 and (*S*)-(+)-2 by Ca(Nph)$_2$ and Ca(BPh)$_2$



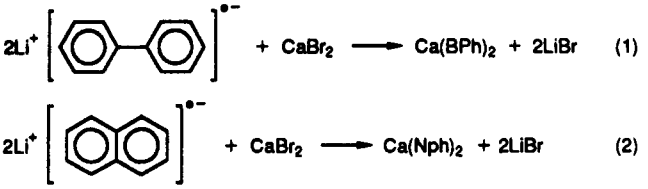
X = Br, (*S*)-(+)-1; X = Cl, (*S*)-(+)-2 → (+)-5 + (+)-6

			% yield (op)[a]		
X	*T*, h	temp, °C	6	5	1 or 2
Cl[b,d]	0.5	−20		45 (0)	55 (100)
Br[b,d]	0.5	−20		100 (0)	
Br[b,e]	0.75	−78	21 (0)	48 (0)	31 (100)
Br[c,e]	0.75	−78	26 (0)	49 (0)	25 (100)

[a] Optical purity. [b] Reaction with Ca(BPh)$_2$. [c] Reaction with Ca(Nph)$_2$. [d] Quenched with H_3O^+. [e] Carbonated.

Mechanism of Organocalcium Formation from Ca–Aromatic Complexes

We next examined the formation of organocalcium reagents by direct reaction of the selected halides with calcium–aromatic complexes. As can be seen from Table I, the reductions of (*S*)-(+)-1-halo-1-methyl-2,2-diphenylcyclopropanes 1 and 2 with calcium–aromatic complexes, generated by reaction of preformed lithium biphenylide (LiBPh$_2$) and lithium naphthalenide (LiNph) in tetrahydrofuran with anhydrous calcium bromide (reactions 1 and 2), yielded after rapid quenching with



dilute hydrochloric acid 1-methyl-2,2-diphenylcyclopropane (5) or, after carbonation of the reaction mixture, the corresponding 1-methyl-2,2-diphenylcyclopropanecarboxylic acid 6. In all cases the products were *completely racemic*. Significantly, the starting material that survived the reaction was recovered and found to be optically pure. The procedure used for determining optical purity of the acids 6 by NMR spectroscopy of their corresponding amide derivatives is described in the Experimental Section. It is also of interest to note that the ratio of the products 5 and 6 was not changed significantly when either Ca(BPh)$_2$ or Ca(Nph)$_2$ was used.

Based on these observations the formation of organocalcium compounds is believed to occur via electron transfer (pathway A) rather than halogen–metal exchange (pathway B) as depicted in Scheme II.

The formation of 1-methyl-2,2-diphenylcyclopropane (5) and 1-methyl-2,2-diphenylcyclopropanecarboxylic acid (6) with complete racemization involves the intermediacy of a cyclopropyl free radical (15) generated by a single electron transfer from the calcium–aromatic complex into the carbon–halogen σ^* antibonding orbital to give the short-lived anion radical 14 which collapses to produce the cyclopropyl radical (pathway A). The latter, being produced in solution, reaches its inversion equilibrium

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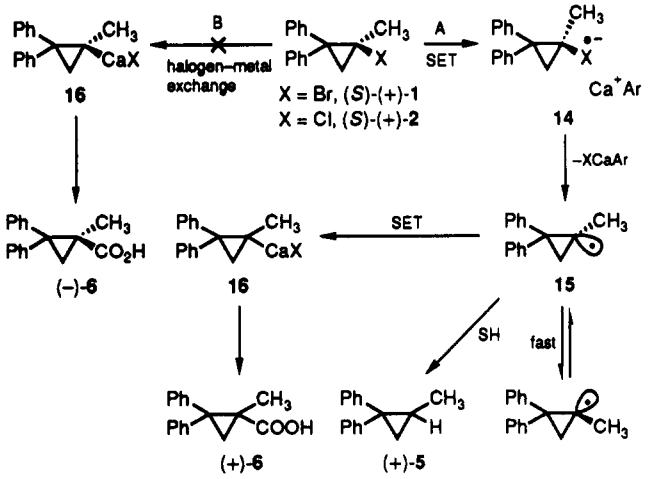
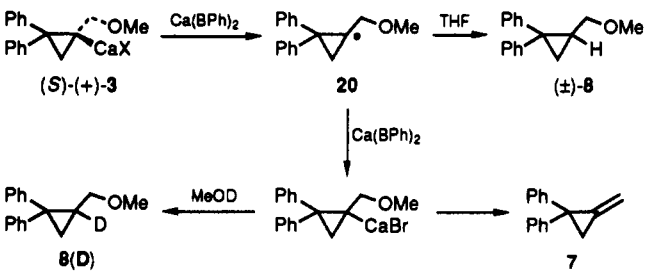
Scheme II



Scheme III



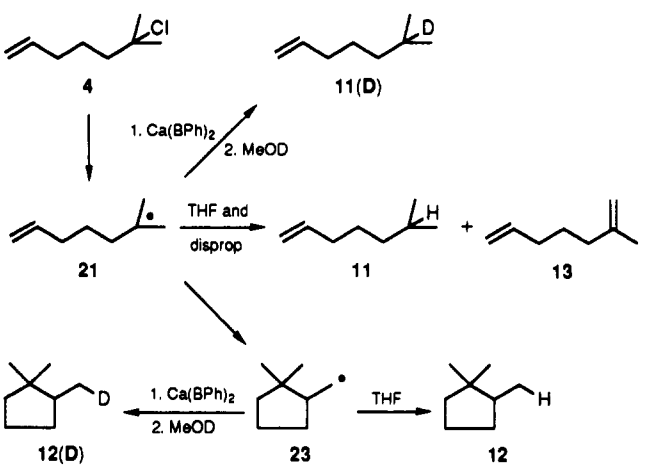
10^{11} s^{-1} before being trapped by a second electron transfer to yield a stable cyclopropylcalcium which when quenched with CO_2 gives the racemic carboxylic acid **6** or by reaction with THF to yield racemic **5**. Reaction of the radical **15** with solvent would also yield racemic hydrocarbon **5**. By contrast, a halogen–metal exchange reaction (pathway B) would be expected to give rise to a configurationally stable organocalcium reagent **16** with complete retention of configuration which after carbonation would yield an optically pure acid. Clearly, this is not the pathway that the reaction takes.

The examination of the stereochemistry and the nature of the products formed during the reduction of (*S*)-(+)-1-bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane (**3**) with calcium–aromatic complexes provides a further illustration that the calcium intermediate formed quickly eliminates methoxide, whereas the radical does not. The reaction of **3** with $Ca(Bph)_2$ was carried out under the same conditions as employed for the reduction of **1**, –60 °C in THF. The reaction mixture was quenched at –60 °C with anhydrous MeOD to yield 48% of 1-methylene-2,2-diphenylcyclopropane (**7**) and 52% of racemic 1-(methoxymethyl)-2,2-diphenylcyclopropane (**8**) which contained less than 5% of deuterium, as detected by mass spectrometry.

These observations are consistent with the formation of radical **18** as an intermediate by single electron transfer as illustrated in Scheme III. As expected radical **18** undergoes rapid inversion and reaction with THF to give racemic **8**. Alternatively, **18** can be reduced by a second electron transfer to give the calcium derivative **19**. The latter, once formed, undergoes mainly elimination of methoxide to give the exocyclic olefin.

These studies based on stereochemical analyses and product distribution, using chiral tertiary cyclopropyl systems as probes, demonstrate that carbon–halogen

Scheme IV



cleavage mediated by Ca–aromatic complexes occurs by electron transfer reactions which produce free radicals in solution (homogeneous condition). We also suggest that the structures of the Ca–biphenyl and the Ca–naphthalene complexes should be viewed as Ca–aromatic anion radicals rather than organocalcium reagents.

In order to further test our mechanistic conclusions, we extended the investigation by using a tertiary alkyl cyclizable radical clock as a probe. Kinetic data concerning reduction of alkyl halides can be obtained from the numerous studies of Saveant et al.[19] These workers concluded that reductive cleavage of the carbon–halogen bond in aliphatic halides, either by direct electrochemical reduction at an inert electrode under heterogeneous conditions, or by electrochemical reduction mediated by an aromatic anion radical, involves a concerted electron transfer–bond breaking mechanism where the origin of the driving force is the standard potential of the $RX/R^{\bullet} + X^-$ and not the $RX/RX^{-\bullet}$ couple. Electron transfer rate constants for the carbon–halogen bond cleavage as well as for the reduction of the radical formed can be obtained from the data presented in their studies.[20] They point out that, in general, the ease of reduction of alkyl radicals is in the order primary > secondary > tertiary.

Reduction of the precursor to the radical clock, 6-chloro-6-methyl-1-heptene (**4**), with Ca–aromatic anion radical (produced from lithium biphenylide) in THF at –60 °C yielded after quenching with MeOD the products shown in Scheme IV.

The main hydrocarbons detected by GC-MS and ^1H NMR were 41% of 1,1,2-trimethylcyclopentane (**12**) (25% of deuterated and 16% of nondeuterated), 51% of the straight chain olefin **11** (5% of deuterated and 46% of nondeuterated), and 2% of diene **13**.

As expected, the relatively stable radical **21** formed after the first electron transfer in this homogeneous reaction underwent competitive reactions. The pseudo-first-order rate constant, at 50 °C, for hydrogen atom abstraction by tertiary alkyl radicals from THF[21] is on the order of 2×10^3 s^{-1}. Since this reaction would be expected to be significantly slower at –60 °C, where we carried out our reactions, this could not be a significant source of the nondeuterated **11**. The deuterium content indicates that

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Table II. Yields of Products Obtained from Radical 21 under a Variety of Conditions

	% yield						
	12	12D	(12 + 12D)	11	11D	13	(11 + 11D + 13)
this work	16	25	41	46	5	2	53
ref 15[a]	1	11	12	10	58	5	73
ref 16[b]	43		43	26		22	48

[a] 4 plus magnesium in THF at 25 °C. [b] Photolysis of 2,2'-azo-2-methyl-6-heptene in ether at 25 °C.

only 5% of radical 21 was reduced to the calcium intermediate. Since only 2% of 11 arises from disproportionation of 21 it is not clear where the remaining 44% of the nondeuterated olefin 11 comes from. If it was not produced by reaction of radical 21 with THF could it have come from reaction of the organocalcium reagent with solvent? Bryce-Smith and Skinner[12f] showed that the decomposition of a primary organocalcium in THF was slow at room temperature. However, tertiary organocalcium reagents, other than cyclopropyl or bridgehead,[11] would be expected to react much faster with THF and this could well be the source of proton in 11.

Of interest is the report by Ingold[22b] that radical 21 cyclizes to the primary (dimethylcyclopentyl)methyl radical 23 with a rate constant on the order of 5×10^3 s^{-1} at −60 °C. Since radical 23 is easier to reduce[19] than the tertiary radical 21, one would expect to obtain a larger amount of calcium derivative from the former. Indeed, this is the case: 25% of deuterated 12 was detected and reaction of radical 23 with solvent gave 16% of 1,1,2-trimethylcyclopentane (12). As can be seen from Table II, this compares well with the results obtained when radical 21 is generated under homogeneous conditions by photochemical decomposition of 2,2'-azo-2-methyl-6-heptene.[16] Studies on Grignard formation reported by Ashby et al.[15] showed that when radical 21 was generated by direct interaction of a *magnesium surface* with 6-chloro-6-methyl-1-heptene (4) in THF (heterogeneous conditions), the main hydrocarbons formed after quenching with MeOD were 68% of the olefin 11 (58% of deuterated and 10% of nondeuterated) and only 11.8% of trimethylcyclopentane 12 (10.7% of deuterated and 1.1% of nondeuterated). In our case the large amount of cyclic product obtained is in agreement with an electron transfer process involving *free radicals in solution.*

Mechanism of the Carbon–Halogen Bond Breaking Effected by Solutions of Ca–Ammonia

The chemical composition and physical properties of solutions of dissolved metal in liquid ammonia are known to depend upon the concentration of these solutions.[5,6] At low concentration of alkali metals, alkaline earths (Ca, Sr, Ba), or lanthanides (Eu, Yb) in liquid ammonia the blue paramagnetic solutions behave as electrolytes containing a solvated electron–metal cation pair. As the concentration is increased the solutions become diamagnetic and assume a bronze metallic luster. The metallic nature of these solutions is due to the donation of one electron in the composition of $M(NH_3)_4$ when M is an alkali metal and two electrons in the composition of $M(NH_3)_6$ when M is an alkaline earth or a lanthanide.

The reduction of chiral 1-halo-1-methyl-2,2-diphenylcyclopropane with sodium in liquid ammonia has been investigated previously in our laboratory.[10] It was shown that the stereochemical results obtained for this reaction were dependent on the concentration of sodium in liquid ammonia, the halogen used, and a heterogeneity factor.

We first examined the reduction of cyclopropyl halides 1 and 2 with dissolving calcium in liquid ammonia at low concentration. At a calcium concentration of 0.4%, the blue paramagnetic solution of Ca–ammonia reduced 1-bromo-1-methyl-2,2-diphenylcyclopropane (1) at the boiling point of ammonia. The only products identified by gas chromatography and NMR spectroscopy were 78% of 1,1-diphenylbutane (9) and 22% of 1,1-diphenyl-2-methylpropane (10). A similar result has been reported during the reduction of 1 with sodium–liquid ammonia at concentrations <1%.[10a] The mechanism proposed (Scheme V) for this opening of cyclopropane ring, in which the cyclopropane hydrocarbon 5 was shown to be the first product formed, was supported by the ability of the *gem*-phenyl groups to accept electrons from the dissolving metal[10b] in order to form the short-lived radical anion 25 which opens quickly to the anion radicals 26 and 27. Addition of a second electron to 26 and 27 gives rise to anions 28 and 29, which were trapped previously by alkylation with benzyl chloride.[10]

The result was different when (*R*)-(+)-1-bromo-1-methyl-2,2-diphenylcyclopropane (1) was treated with metallic bronze $Ca(NH_3)_6$ in THF at −30 °C until −10 °C. The reaction gave mainly (*S*)-(+)-1-methyl-2,2-diphenylcyclopropane (5), in 81% yield, $[\alpha]_{Hg}$ +16° (*c* 0.9, $CHCl_3$) which corresponds to 11% of retention of configuration mixed with 8% of 1,1-diphenylbutane (9) and 7% of a mixture of isomers in which one of the phenyl groups of 5 has been partially reduced. It should be noted that when the same reaction was repeated at room temperature, only the isomeric mixture derived from partial reduction of the *gem*-phenyls was formed, presumably by a Birch-type reduction.

An interesting effect of halogen was observed during the course of this reduction. (*S*)-(+)-1-Chloro-1-methyl-2,2-diphenylcyclopropane (2) when treated with metallic bronze $Ca(NH_3)_6$, at −30 °C to −10 °C, in THF yields 64% of (*R*)-(−)-1-methyl-2,2-diphenylcyclopropane (5), $[\alpha]_{Hg}$ −43° (*c* 1, $CHCl_3$), which corresponds to 29% of retention of configuration. The mixture also contained 7% of 1,1-diphenylbutane (8), 6% of an isomeric mixture of phenyl reduction products, and 14% of optically pure starting material 2.

The amount of retention observed is consistent with the fact that the metallic bronze $Ca(NH_3)_6$ behaves like a solid surface from which an electron is transferred to the σ^* antibonding orbital. This leads to a short-lived anion radical–cation radical pair which can either collapse to yield the corresponding organocalcium derivative with retained stereochemistry or dissociate at the surface to yield the R··CaX radical pair which can combine to form racemic RCaX (Scheme VI). The organocalcium intermediate is quickly quenched by ammonia to yield the corresponding hydrocarbon. We have previously shown in the case of the carbon–halogen bond cleavage caused by electron transfer from a metallic surfaces such as Li[23]

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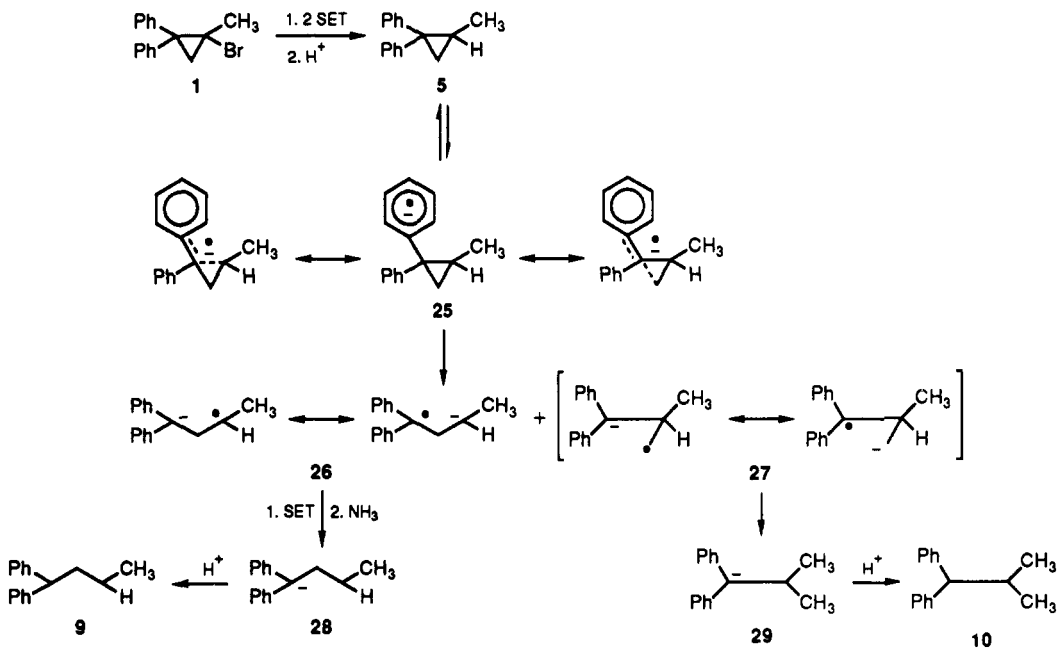
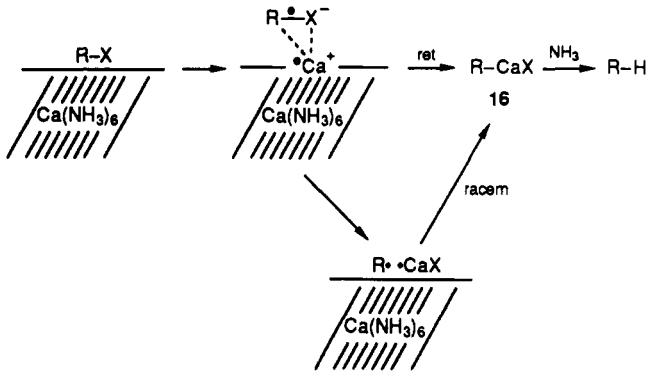
Scheme V



Scheme VI



and Mg[24] that the retention observed arises from the collapse of the radical anion on the surface of the metal. It is also of interest to note that the effect of the halogen on the optical purity of the hydrocarbon which decreases in going from chloride (29%) to bromide (11%) is also observed in the reaction of 1 and 2 with lithium and magnesium surfaces.

In summary, the studies reported here establish that the formation of organocalcium reagents by the direct reaction of organic halides with calcium–aromatic complexes such as calcium–biphenyl ($Ca(BPh)_2$) and calcium–naphthalene ($Ca(Nph)_2$) takes place by a single electron transfer mechanism which provides free radicals in solution as intermediates.

We have also demonstrated that the carbon–halogen bond cleavage effected by the calcium–ammonia complex $Ca(NH_3)_6$ occurs on the surface of the metallic luster by an electron transfer process involving the formation of a tight anion radical–cation radical pair as an intermediate.

Experimental Section

All the reagents were purchased from Aldrich, except for calcium bromide and calcium turnings which were purchased from CERAC and J.T. Baker, respectively. THF, ether, and DME were dried by refluxing and distilling from sodium–potassium alloy. *tert*-Butyllithium was titrated before use.

^1H NMR spectra were recorded at 300 MHz in $CDCl_3$ with Me_4Si and $CHCl_3$ (7.26 ppm) as internal standards. Mass spectra and GC-MS analyses were performed using a Finnigan 4500 automated gas chromatograph/EI-CI mass spectrometer equipped with a DB-5 fused silica capillary column (J&W Scientific). Preparative GC were performed on a Varian Aerograph Model 700 gas chromatograph with 15% SF-96 on chromosorb W as the stationary phase.

Microanalyses were performed by Beller Laboratories, Göttingen, Germany. Optical rotations were measured at either the 546.1-nm mercury line or the 589.3-nm sodium line by using a Bendix Model DR-1 digital display. The cell length was 0.17 dm, and all solvents used were of spectrophotometric grade. Percent optical purity was determined as the observed specific rotation divided by the maximum specific rotation multiplied by 100.

Thin-layer chromatography (TLC) was performed by using glass plates coated with Merck silica gel 60 PF-254 + 366. Flash chromatography[26] was carried out by using silica gel 60 F_{254} (70–230 mesh, E. Merck).

Optically Active (1-Methyl-2,2-diphenylcyclopropyl)-calcium Bromide (16). To a solution of (*S*)-(+)-1-bromo-1-methyl-2,2-diphenylcyclopropane[13] (1) [118 mg (0.41 mmol), $[\alpha]^{25}_{Hg}$ +119° (*c* 1, $CHCl_3$, 91% optically pure)], in 4 mL of dry ether, under argon at −78 °C was added a solution of *tert*-butyllithium (1.57 M) in pentane (0.55 mL, 0.86 mmol) dropwise. After complete addition the mixture was stirred at −78 °C for 30 min. Calcium bromide (0.4 g, 2.05 mmol) was added portionwise under a flow of argon. The mixture was allowed to slowly reach −15 °C and kept at this temperature for 1.5 h and then treated

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with 1 mL of dry DME. After 15 min at −15 °C the resulting orange mixture was carbonated by pouring onto freshly powdered dry ice at −78 °C for 1 h. The reaction mixture was allowed to reach room temperature, poured onto a mixture of ice and hydrochloric acid, and extracted with ether. The organic layers were combined, washed with saturated NaCl, and dried over anhyd $MgSO_4$ and the solvent was evaporated in vacuo. The ^1H NMR spectrum of the crude acid showed it to be a mixture of 5 and 6 in 27:73 ratio. The mixture was diluted with ether and extracted with 10% NaOH. The base extracts were washed with ether and neutralized with 10% acid, and the acidic solution was extracted with ether. The ether layers were washed with saturated NaCl and dried over anhyd $MgSO_4$. Removal of the solvent in vacuo gave 26 mg (25%) of 1-methyl-2,2-diphenylcyclopropanecarboxylic acid (6), $[\alpha]^{25}_{Hg}$ −36.4° (c 0.32, $CHCl_3$, ee = 84%),[13] 97% retention of configuration.

The ether extracts were washed with 10% NaOH and with saturated NaCl and dried over anhyd $MgSO_4$ and the ether was evaporated in vacuo. Flash chromatography (silica, pentane) gave 59 mg (69%) of 1-methyl-2,2-diphenylcyclopropane (3), $[\alpha]^{25}_{Hg}$ −121° (c 0.82, $CHCl_3$, ee = 81%),[13] 90% retention of configuration.

Reaction of (*S*)-(+)-1-Bromo-1-methyl-2,2-diphenylcyclopropane (1) with $Ca(BPh)_2$. To a solution of 590 mg (3.83 mmol) of biphenyl in 5 mL of dry THF was added lithium metal (24 mg, 3.48 mmol) under an argon atmosphere. The mixture was stirred at room temperature until the lithium was completely consumed (ca. 2 h). The green solution of lithium biphenylide was transfered via a cannula into a suspension of excess $CaBr_2$ (553 mg, 2.77 mmol) in 3 mL of dry THF. The reaction mixture was stirred for 1.5 h at room temperature and then cooled to −78 °C. (*S*)-(+)-1-Bromo-1-methyl-2,2-diphenylcyclopropane[13] (1) (250 mg, 0.87 mmol), $[\alpha]^{25}_{Hg}$ +119° (c 1, $CHCl_3$, 91% optically pure) was added, as a solid, at −78 °C. After 45 min of stirring, the orange mixture was carbonated by passing a stream of CO_2 through the solution at −78 °C. The reaction mixture was allowed to reach ambient temperature, poured onto a mixture of ice and hydrochloric acid, and extracted with ether. The organic layers were combined, washed with saturated NaCl, and dried over anhyd $MgSO_4$, and the solvent was evaporated in vacuo. ^1H NMR analysis of the crude mixture showed it to be a mixture of 1, 5, and 6 in a ratio of 31:48:21. The mixture was diluted with ether and extracted with 10% NaOH.

The base extracts were washed with ether, neutralized with 10% acid, and extracted with ether. The ether layer was washed with saturated NaCl and dried over anhyd $MgSO_4$. Removal of the solvent in vacuo gave 41 mg of 1-methyl-2,2-diphenylcyclopropanecarboxylic acid[13] (6), $[\alpha]^{25}_{Hg}$ 0 ± 3° (c 0.75, $CHCl_3$), 0% retention of configuration. IR and ^1H NMR spectra were identical to those of authentic 1-methyl-2,2-diphenylcyclopropanecarboxylic acid. The acid was converted to the corresponding amide by first dissolving it in 5 mL of CH_2Cl_2 and adding a slight excess of a 2 M solution of oxalyl chloride in CH_2Cl_2 and a drop of DMF. After 0.5 h of stirring at room temperature, the solvent and excess of oxalyl chloride were removed in vacuo, and the residue was dissolved in CH_2Cl_2 and treated with 2 equiv of (*S*)-(−)-α-methylbenzylamine at 0 °C for 2 h. The solution was poured onto a mixture of ice and HCl and extracted with ether. The ether layers were combined and washed with 5% HCl and saturated NaCl and dried over anhyd $MgSO_4$ and the solvent was evaporated in vacuo. The diastereoisomeric excess (de = 0 ± 2%) could be easily measured by ^1H NMR either from the signals corresponding to the cyclopropyl protons or from those corresponding to methyl groups. An authentic sample was prepared from a mixture of (*R*)-(−)- and (*S*)-(+)-1-bromo-1-methyl-2,2-diphenylcyclopropane[13] in an 80:20 ratio, by treating the mixture with 2 equiv of *tert*-butyllithium in ether at −78 °C followed by carbonation and conversion to the amide with (*S*)-(−)-α-methylbenzylamine as described above. ^1H NMR: diastereoisomer (*R*–*S*) δ 1.23 (s, 3 H), 1.36 (d, *J* = 7 Hz, 3 H), 1.41 (d, *J* = 5 Hz, 1 H), 2.1 (d, *J* = 5 Hz), 4.92 (m, 1 H), 5.68 (d, 1 H), 7.1–7.45 (m, aromatics); diastereoisomer (*S*–*S*) δ 1.06 (d, *J* = 6.5 Hz, 3 H), 1.214 (s, 3 H), 1.45 (d, *J* = 5.4 Hz, 1 H), 2.05 (d, *J* = 5.5 Hz, 1 H), 5.9 (m, 1 H), 5.5 (d, 1 H), 7.1–7.45 (m, aromatics).

The ether extracts were washed with 10% NaOH and with saturated NaCl and dried over anhyd $MgSO_4$, and the ether was evaporated in vacuo. Flash chromatography (silica, pentane) yielded 60 mg of optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane[13] (1), $[\alpha]^{25}_{Hg}$ +115° (c 0.5, $CHCl_3$, 97% retention of configuration), and 65 mg of 1-methyl-2,2-diphenylcyclopropane[13] (5) was separated from the biphenyl using preparative gas chromatography (180 °C), $[\alpha]^{25}_{Hg}$ 0 ± 3° (c 0.87, $CHCl_3$, 0% retention).

Reaction of (*S*)-(+)-1-Bromo-1-methyl-2,2-diphenylcyclopropane (1) with $Ca(Nph)_2$. The reaction was conducted under the same conditions as above using Li–Nph as a source of highly reactive calcium rather than Li–BPh. The products of the reaction were isolated and analyzed using the same technique as above to give 49% 1-methyl-2,2-diphenylcyclopropane (5), $[\alpha]^{25}_{Hg}$ 0 ± 3° (c 0.5, $CHCl_3$, 0% retention), and 26% of racemic acid 6 admixed with 25% of starting cyclopropyl bromide 1 with retained optical purity and configuration.

Reaction of (*S*)-(+)-1-Chloro-1-methyl-2,2-diphenylcyclopropane[13] (2) with $Ca(BPh)_2$. The reaction was conducted following the procedure described above. The cyclopropyl chloride 2, $[\alpha]^{25}_{D}$ +64° (c 1, $CHCl_3$), was added at −78 °C and the reaction mixture was allowed to warm to −20 °C for 1.5 h and then quenched with a 10% solution of HCl. After workup, the ^1H NMR and analytical gas chromatography of the crude product indicated the presence of 45% of 1-methyl-2,2-diphenylcyclopropane (5) mixed with 55% of starting material 2. After isolation, 5 was shown to be completely racemic, while the cyclopropyl chloride 2 was recovered with the same optical activity and configuration.

Reaction of (*S*)-(+)-1-Bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane[14] (3) with $Ca(BPh)_2$. Cyclopropyl bromide 3 was added to the highly reactive $Ca(BPh)_2$ at −60 °C. The reaction mixture was stirred for 1 h at −60 °C and then quenched with MeOD (>99.5% *d*). After workup the mixture was analyzed by ^1H NMR and GC-MS showing the following compounds: 48% of 1-methylene-2,2-diphenylcyclopropane[14] (7) and 52% of 1-(methoxymethyl)-2,2-diphenylcyclopropane[14] (8) that had incorporated less than 5% of deuterium. The latter was purified by flash chromatography and was shown to be completely racemized.

Reaction of 6-Chloro-6-methyl-1-heptene[15a] (4) with $Ca(BPh)_2$. 6-Chloro-6-methyl-1-heptene (4), 200 mg (1.4 mmol), was injected at −60 °C to a solution of highly reactive $Ca(BPh)_2$. The reaction mixture was stirred at −60 °C for 30 min, allowed to warm to −30 °C for 15 min more, and quenched at this temperature with MeOD. Pentane (50 mL) was added to the mixture and the organic layer was washed with a 10% solution of HCl and saturated NaCl and dried over anhyd $MgSO_4$, and the solution was analyzed by GC-MS. The solvent was removed by distillation through a spinning band column and the residue was analyzed once more by ^1H NMR. The analyses and comparison with authentic samples showed that the reaction proceeded with 57% conversion. The hydrocarbons formed were mainly 46% of olefin 11,[16] 5% of deuterated 11, 16% of cyclopentane 12,[16] 25% of deuterated 12, and 2% of diene 13.[16]

Preparation of Diluted Solution of Calcium–Liquid Ammonia. Ammonia (250 mL) was first dried by passing it through solid KOH pellets and then distilled from a sodium–ammonia solution into a three-necked flask provided with a dry ice condenser connected to a mercury bubbler pressure release, a curved addition tube for adding the calcium, and a dry ice bath. Calcium (1 g) was added to the ammonia and the dry ice bath was removed to allow the solution to warm to the boiling point of ammonia. The blue solution was stirred for 1 h. During that time the volume of the solution, as determined by a scratch mark on the flask, was kept at 250 mL (0.4%).

Reduction of (*R*)-(−)-1-Bromo-1-methyl-2,2-diphenylcyclopropane (1) with a Dilute Solution of Calcium–Ammonia. Optically pure cyclopropyl bromide 1, 290 mg (mmol), $[\alpha]^{25}_{Hg}$ −128° (c 1, $CHCl_3$), was added to the blue solution of calcium–ammonia, and the reaction mixture was stirred for 1 h. Then 300 mL of pentane was added and the ammonia was allowed to evaporate. The pentane solution was washed with saturated NH_4Cl and dried over anhyd $MgSO_4$. The solvent was removed in vacuo and the residue was analyzed by ^1H NMR and analytical gas chromatography to give 78% of 1,1-diphenylbutane[10] (9) and

22% of 1,1-diphenyl-2-methylpropane[10] (10). Preparative gas chromatography (180 °C) yielded pure 9 and 10 which showed the same NMR spectra as their authentic samples.

Preparation of the Metallic Bronze $Ca(NH_3)_6$. Calcium (3 g, 75 mmol) was dissolved in 100 mL of dry liquid ammonia as described above. The blue solution was allowed to warm under argon pressure in order to evaporate the ammonia through a bubbler without exposing the mixture to air. A bronze mirror was formed on the flask wall. After about 2 h the ammonia, checked by pH paper, was completely evaporated. The bronze solid was cooled to −20 °C and 40 mL of dry THF was added under an argon atmosphere.

Reduction of (*R*)-(+)-1-Bromo-1-methyl-2,2-diphenylcyclopropane (1) with Metallic Bronze $Ca(NH_3)_6$. Optically pure cyclopropyl bromide 1, $[\alpha]_{Hg}$ −128° (*c* 1, $CHCl_3$), 1 mmol (290 mg), was added in one portion to the reaction mixture at −30 °C. The heterogeneous mixture was kept at this temperature for 1 h and then allowed to warm to −10 °C for 30 min more. Hexane (100 mL) was added and the reaction mixture was hydrolyzed by slowly adding a cold solution of saturated NH_4Cl. Extraction with hexane gave a crude product which was analyzed by NMR and separated by preparative GC (200 °C) to give the following products: 81% of diphenylcyclopropane 5, $[\alpha]^{25}_{Hg}$ +16° (*c* 0.9, $CHCl_3$, 11% retention), 8% of 1,1-diphenylbutane (9), and 7% of a mixture of isomeric products in which one of the phenyl groups in 5 has been partially reduced.

Repeating this reaction at room temperature gave only a mixture of several isomers which arose from phenyl ring reduction. The ^1H NMR spectra showed the presence of vinyl and cyclopropyl protons, but all attempts to separate the mixture of isomers using either preparative GC or flash chromatography were unsuccessful.

Reaction of (*S*)-(+)-1-Chloro-1-methyl-2,2-diphenylcyclopropane (2) with $Ca(NH_3)_6$. The reaction was carried out in THF as described above at −30 to −10 °C to give 64% of diphenylcyclopropane 5, $[\alpha]^{25}_{Hg}$ −43° (*c* 1, $CHCl_3$, 29% retention), 7% of 1,1-diphenylbutane (9), 6% of a mixture of phenyl reduction isomeric products, and 14% of optically pure starting material.