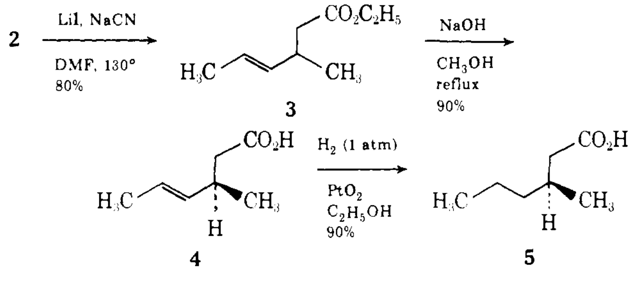
Table I

Ligand	P(N)/Pd[e]	Conditions, °C	Time, hr	Rotation of product, deg 2 (*c*, $CHCl_3$)	3 (*c*, $CHCl_3$)	4 (*c*, $CHCl_3$)	5 (*c*, benzene)	Opt yield, %
(+)-DIOP	4/1	0, then 25	1, then 2	−3.64 (22.0)		−4.47 (5.88)	−0.34 (2.94)	12.2 ± 0.8[a] (13.4 ± 2.8)[b]
(+)-DIOP	4/1	−40, (H_2O) 25	9.5, 16	−6.42 (3.16)				22.4 ± 2.2[c]
(+)-DIOP	4/1	−78, (H_2O) 25	72, 1	−5.15 (6.08)				17.9 ± 1.8[c]
(+)-ACMP	2/1	25	0.5	−4.11 (1.36)				17.9 ± 1.8[c,d]
(+)-ACMP	2/1	−40, (H_2O) 25	9, 16	−5.38 (25.0)	−4.74 (9.50)	−7.10 (4.29)		24.4 ± 1.6[a,d]
(+)-ACMP	2/1	−78, (H_2O) 25	72, 4	−5.15 (2.35)				22.4 ± 2.8[c,d]
(−)-Sparteine	4/1	25	2	−5.81 (3.13)				20.2 ± 2.1[c]
(−)-DMIP	4/1	0, 25	1, 3	−0.59 (2.54)				2.0 ± 0.3[c]

[a] Based on maximum rotation range for **4** of 39.6–34.5°.[11a] [b] Based on maximum rotation for **5** of 2.5°.[11b] [c] Based on maximum rotation range for **2** of 26.1–31.9° calculated from range of **4**. [d] Corrected for 80% optical purity of (+)-ACMP. [e] The ratio of the number of phosphorus (or nitrogen) atoms of the ligand to the number of palladium atoms of the complex.

3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(+)-DIOP],[8] (+)-*o*-anisylcyclohexylmethylphosphine [(+)-ACMP],[9] dimenthylisopropylphosphine [(−)DMIP],[4,10] and (−)-sparteine produced the allylic alkylation product **2** optically active. Table I summarizes the data.

To determine the optical purity and absolute configuration of the product, correlation with *trans*-3-methyl-4-hexenoic acid and 3-methylhexanoic acid of known absolute configuration[11] was carried out. Treatment of **2** with lithium iodide and sodium cyanide in hot dimethylformamide[12] effected decarboethoxylation to **3**. Hydrolysis produced the unsaturated acid **4** (identical in all respects with an authentic sample[11a]) for which a maximum rotation of 34.5–39.6° has been reported.[11a] Hydrogenation of **4** gave the saturated acid **5** for which a maximum rotation of 2.5° has been reported.[11b] It has been further established that dextrorotatory **4** has the *R* configuration. Based upon these data, allylic alkylation produced the *S* isomer with optical yields ranging from 2 to 24% (see Table I). The data indicate that the proximity of the asymmetry to the complexing atom in the ligand rather than steric bulk plays the dominant role. Thus, sparteine and ACMP give higher optical yields than DIOP and DMIP with the last ligand giving the lowest. As generally observed, decreasing the temperature increases the optical induction although going to −78° has a deleterious effect. Such a result suggests that at this low temperature carbon–carbon bond formation may not be occurring (but carbon–palladium bond formation may have occurred[13]). Formation of the final product then takes place during the subsequent warm-up after aqueous quenching.



The optical yields obtained in this case are among the highest known for such carbon–carbon bond formation with the exception of the oligomerization reaction of Wilke and coworkers.[4] Such an achievement illustrates another unique feature of the allylic alkylation method.

Acknowledgment. We wish to thank Dr. William S. Knowles for a generous gift of (+)-ACMP, Professor Günther Wilke for a generous gift of (−)-DMIP, and Professor Richard Hill for an authentic sample of ethyl *trans*-3-methyl-4-hexenoate. We also express our gratitude to the National Institutes of Health and the National Science Foundation for their generous support of our work.

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Radical Reduction with Naphthalenide Ion and Evidence for Carbanion Oxidation by Halides

Sir:

The reaction of sodium naphthalenide with organic halides has been shown to produce organic radicals plus halide ions *via* electron transfer from the radical anion to the halide.[1–5] Although simple alkyl radicals may abstract a hydrogen atom from ether solvents,[1f] resonance stabilized benzylic radicals described below were found to undergo coupling to dimers or reduction to carbanions by eq 1 faster than atom transfer from the solvent.

$$R\cdot + C_{10}H_8\cdot^- \longrightarrow R:^- + C_{10}H_8 \qquad (1)$$

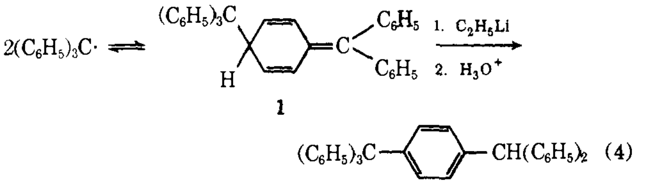
Bimolecular coupling of radicals may occur directly or by a subsequent reoxidation of the carbanion by halide (eq 2) as was proposed recently.[1a]

$$R:^- + RX \longrightarrow 2R\cdot \longrightarrow RR \qquad (2)$$

During naphthalenide ion reduction experiments on benzylic halides, we observed stoichiometric formation of triphenylmethyl radicals from trityl chloride and lithium naphthalenide regardless of the order of mixing the reagents. This independence of the order of addition during titrations suggests that trityl chloride oxidizes trityl carbanion to a radical in a single electron transfer process.

Titrimetric addition of triphenylmethyl chloride (0.2174 g/ml) to 1 equiv of lithium naphthalenide (0.039 mol) in tetrahydrofuran (50 ml) produces 1 equiv of triphenylmethyl radicals which dimerize to form 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene (**1**).[6] See eq 3 and 4.

$$(C_6H_5)_3CCl + Li^+C_{10}H_8\cdot^- \longrightarrow (C_6H_5)_3C\cdot + Cl^- + C_{10}H_8 \qquad (3)$$



1

2

(4)

The end point can be observed upon the disappearance of the green colored naphthalenide ion whereupon the yellow color of the trityl radical is detected. After cooling to −78°, the equilibrium of eq 4 is shifted strongly toward the dimer, **1**. Isomerization of **1** to *p*-benzhydryltetraphenylmethane (**2**)[6,7] was accomplished in 98.5% yield with ethyllithium and water.

When trityl chloride was added to an excess of napthalenide (>2 equiv/equiv RCl) the trityl radicals were reduced to carbanions before they could couple. See Table I.

Table I. Lithium Naphthalenide[a] Reduction of Benzylic Halides

Compound[b]	Mol ratio $ArH\cdot^-/RX$	% RR	% RH
Ph_3CCl	1	100[c]	0
Ph_3CCl	3	0	100[c]
Ph_3CBr	1	100[c]	0
Ph_2CHCl	1	78[c]	18[d]
Ph_2CHCl	2.27	41.7[c]	51.2[d]
$PhCHCl$	3	19[d]	71[d]
$PhCH_2Cl$	1	72[d]	16[d]
$PhCH_2Cl$	3	22[d]	

[a] 0.39 *M* in THF. [b] 0.7–1.34 *M* in THF; halide is added slowly to $ArH\cdot^-$. [c] By isolation. [d] By quantitative gas chromatography on a Hewlett-Packard 5754B.

In titrations of equivalent quantities of lithium naphthalenide with benzhydryl chloride, *sym*-tetraphenylethane (**3**, 70–78%), was produced. The formation of **3** may occur either by coupling of benzhydryl radicals or by SN2 displacement between diphenylmethyllithium and benzhydryl chloride. However, the slow inverse addition of 1 equiv of naphthalenide ion to benzhydryl chloride also produces **3** (75%) under conditions where halide is in excess and no carbanion formation can be detected visually. Under these conditions, radical coupling must be the predominant pathway for the formation of **3**.

Lithium naphthalenide cleaves **3** rapidly as reported by Eisch.[8] Equivalent quantities reacting for 1 hr showed 42% of **3** unchanged.

Similar titrations of 1 equiv of lithium naphthalenide with 1 equiv of benzyl chloride gave 72% of bibenzyl, **4**.[3d]

During the titration of 1 equiv of 0.78 *M* trityl chloride to 0.78 *M* lithium naphthalenide, the red color of the triphenylmethyl carbanion could be discerned in the dark naphthalenide solution. The fact that both the red and the green color were discharged rapidly with a single drop of halide solution at the end point suggested that trityl chloride rapidly oxidizes triphenylmethyllithium to trityl radicals *via* electron transfer (eq 2). Verification was secured through preparation of authentic triphenylmethyllithium by metalation of triphenylmethane with *n*-butyllithium.[9] Titration of trityl carbanion with trityl chloride until discharge of the carbanion color quantitatively produced **1** as judged by the isolation of 1 mol of **2** for each mole of trityl chloride added.[10]

Clearly triphenylmethyl chloride reacts with triphenylmethyl carbanion *via* a one-electron oxidation process to produce 2 mol of trityl radicals. The best analogy for the present electron transfer oxidation of trityl carbanion by trityl halide is found in the work of Korn-

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(10) Inverse order of addition experiments in which trityl carbanion is added to trityl chloride produced 1 mol of **1** for each mole of added carbanion.

blum[11,12] and Russell[13] who have demonstrated that a radical anion chain mechanism operates in oxidation of 2-nitropropane lithium salts by compounds such as p-nitrocumyl chloride and α,p-dinitrocumene.[11]

The question arises whether diphenylmethyl halides react in a similar manner with triphenylmethyl carbanion?

Treatment of triphenylmethyllithium with benzhydryl bromide (3.55 g, 0.0143 mol) produced pentaphenylethane, **5** (5.58 g, 95%).[14] Use of benzhydryl chloride also produced pentaphenylethane in 91% yield. These reactions appear to involve either simple nucleophilic displacement[19] or formation of a pair of radicals in a cage,[1h] from which benzhydryl and trityl radicals do not escape, for if any free benzhydryl or trityl radicals were formed, *sym*-tetraphenylethane and **1** would have been produced.

In order to show that cross coupling products would form from mixtures of benzhydryl and trityl radicals, competition experiments using 1 equiv of equimolar benzhydryl and trityl halides solution with 1 equiv of lithium naphthalenide were run. After discharge of the aromatic radical anion color, oxygen was bubbled through the mixture to convert residual trityl radicals into bis(triphenylmethyl) peroxide (18% isolated). Pentaphenylethane (36%) and tetraphenylethane (32%) were isolated.

Comparison of the competition experiments with naphthalenide ion with the triphenylmethyllithium–diphenylmethyl halide reactions leads us to conclude that diphenylmethyl halides do not oxidize triphenylmethyl carbanion by a single-electron transfer process that produces free trityl and benzhydryl radicals.

The question of whether trityl halides react with diphenylmethyllithium to produce radical intermediates was studied. Diphenylmethyllithium was titrated with benzhydryl chloride (6.19 g, 0.0305 mol), to give *sym*-tetraphenylethane (10.2 g, 97.2%).

Reaction of diphenylmethyllithium and triphenylmethyl chloride was followed by quenching with oxygen and gave predominantly **5** (60%) together with **3** (6.%), bis(triphenylmethyl) peroxide (6.6%) and benzhydryl and trityl chlorides. These results are in harmony with rapid establishment of a halogen–metal interconversion equilibrium. This equilibrium lies well to the right as judged by the low yields of peroxide and **3**. If single-electron transfer oxidation of the primary reactants was occurring to any significant extent the yields of **3**, **5**, and peroxide should be comparable not only in absolute amounts but also to the results from the naphthalenide ion competition experiments. The fact that they are not statistically equivalent leads to the conclusion that coupling of free radical intermediates is not the mechanism for formation of **3** and **5** from diphenylmethyllithium. This conclusion finds experimental support in the work of Sommer who has shown that benzhydryllithium reacts with (−)-α-phenylethyl chloride with 100% inversion of configuration to give (−)-1,1,2-triphenylpropane.[19]

The most surprising result in Table I is that a threefold molar excess of lithium naphthalenide reacting with benzhydryl halide does not completely suppress the formation of **3** either by reducing benzhydryl radicals to carbanions faster than they can couple or by cleaving **3** after it is formed. The implication is that benzyhydryl radical is not reduced by naphthalenide ion at diffusion-controlled rates or that benzhydryl anion reacts with benzhydryl halide at a rate competitive with that of lithium naphthalenide. It is hard to imagine an S$_N$2 displacement by benzhydryl anion on benzhydryl halide which can operate at a rate competitive with reduction by naphthalenide. Perhaps oxidation of benzhydryl anion by the halide can produce two radicals with the same speed as naphthalenide ion reduction of a radical.

The other significant result reported here is that naphthalenide ion reacts indiscriminately with an equimolar mixture of trityl chloride and benzhydryl chloride to produce mixtures of radicals which couple statistically forming **3** and **5**.

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(14) Satisfactory microanalysis, mass spectral, and pmr data support this structure. Furthermore, this sample is identical with that obtained following Bachmann's procedure[15] for **5** from triphenylmethylmagnesium bromide and benzhydryl bromide in ether–benzene. The melting points of **5** vary from 145–148° to 178–179° with decomposition in general agreement with literature values[15,16] and the known thermal instability of **5**.[17] Molecular oxygen was bubbled through a benzene solution of **5** for 3 hr at 25° and **5** was recovered quantitatively. The reported reaction[18] of O$_2$ with **5** at 80° probably depends upon prior thermal decomposition of **5**.

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(20) National Science Foundation Undergraduate Research Participant: (a) 1970–1971; (b) 1971–1972.

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Evidence for an Electron-Transfer Component in a Typical Nucleophilic Displacement Reaction

Sir:

Whereas electron-transfer has been noted in a variety of nucleophilic reactions,[1] it has not always been clear what driving forces are operative[1d,e,f] nor in what way electron processes contribute to a nonbiased, typical

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