mmol) of cyclohexanecarbonyl chloride in 3 ml of THF was then added quickly. The temperature of the reaction mixture rose 15 °C and the still turbid mixture was stirred for 20 min at −65 °C. It was then allowed to warm to −10 °C and the cloudy solution was added to 35 g of ice and shaken for 10 min (to destroy any unreacted carbonyl chloride) and then acidified with 20 ml of 2 M HCl and extracted with ether, which was dried ($MgSO_4$) and evaporated under reduced pressure to an orange oil. This was heated (130 °C) in a flask equipped with a reflux condenser until evolution of gas ceased. This oil (containing much HMPA) was then steam distilled to yield 0.732 g of yellow oil. Column chromatography (SiO_2, 1:50 ether–pentane) yielded 60 mg (5% yield) of cyclohexyl methyl ketone [NMR ($CDCl_3$) δ 1.1–2.0 (m, 10 H, $-CH_2-$), 1.1–1.6 (b, 1 H, CHCO), 1.18 (s, 3 H, $COCH_3$); IR (neat) 1715 cm^{-1}].

Reaction of the Dianion of Cyclobutanecarboxylic Acid with Cyclopropanecarbonyl Chloride. When the general procedure is followed, a 23% yield of the keto acid ammonium salt is obtained. When the procedure was modified so that when the reaction mixture was poured on ice, the aqueous portion was washed five times with pentane, which was then dried ($MgSO_4$), concentrated, cooled (−78 °C), and filtered (−78 °C), a 51% yield (0.855 g) of *N,N*-diisopropylcyclopropanecarboxamide was isolated [mp 20–22 °C; NMR ($CDCl_3$) δ 0.6–0.8 (m, 4 H), 1.28 (d, J = 6 Hz, 12 H), 1.56 (b, 1 H), 3.25–4.20 (m, 2 H); IR (neat) 1630 cm^{-1} (b)]. Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31. Found: C, 70.98; H, 11.20.

Registry No.—**2** (R_2 = C_6H_{11}), 61288-77-5; **2** (R_2 = C_5H_9), 61288-76-4; **2** (R_2 = C_4H_7), 61288-75-3; **2** (R_1 = Me; R_2 = Me), 57344-34-0; **2** (R_1 = R_2 = Et), 61259-24-3; **2** (R_1 = H; R_2 = Ph), 56842-55-8; **2** (R_1 = H; R_2 = Me), 60334-04-5; **2** (R_1 = R_2 = H), 60419-47-8; **10**, 61259-25-4; **11** (R = C_6H_5), 61259-26-5; **11** (R = CH_3), 61259-27-6; **12**, 61259-28-7; cyclohexyl benzyl ketone, 61259-29-8; cyclohexyl ethyl ketone, 1123-86-0; cyclohexyl methyl ketone, 823-76-7; *N,N*-diisopropylcyclopropanecarboxamide, 61259-30-1; lithium diisopropylamide, 4111-54-0.

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(3) National Defense Education Act Fellow, 1972–1974.
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Rhodium-Mediated Alkylation of Acid Chlorides. A Facile Solid State Ketone Synthesis Using a Recyclable Polymer-Bound Rhodium Complex

Charles U. Pittman, Jr.,* and Ronnie M. Hanes

Department of Chemistry, University of Alabama, University, Alabama 35486

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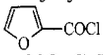
Polymer-bound bis(triphenylphosphine)chlorocarbonylrhodium(I) was found to be a regeneratable reagent for the synthesis of ketones from acid chlorides and organolithium reagents. $RhCl(CO)(PPh_3)_2$ was anchored to diphenylphosphinated styrene–divinylbenzene resins by ligand exchange. Treatment of these resins with organolithium, in THF, at −78 °C, gave $(Ⓟ\text{-}PPh_2)_2RhR(CO)$. The resin was then treated with an acid chloride which oxidatively added giving the anchored rhodium(III) complex, $(Ⓟ\text{-}PPh_2)_2Rh^{III}Cl(R'CO)(R)(CO)$. Upon warming, reductive elimination gave ketone, R'COR, and $(Ⓟ\text{-}PPh_2)_2RhCl(CO)$ was regenerated. Using this method, alkyl or aryl organolithium reagents could be selectively added to the acid chloride function in the presence of cyano, aldehyde, or ester functions. The polymer-bound reagent, $(Ⓟ\text{-}PPh_2)_2RhCl(CO)$, is much easier to handle, separate from reaction mixtures, and recycle than is $(RhCl(CO)(PPh_3)_2$.

The reaction of an acid chloride with either an organolithium reagent or a Grignard reagent is complicated by the fact that the ketone, resulting from the initial reaction, can further react to produce tertiary alcohols. Thus, poor ketone yields are usually achieved using this route (eq 1).

$$R'COCl + RM \rightarrow R'COR \rightarrow R'C(OH)R_2 \qquad (1)$$

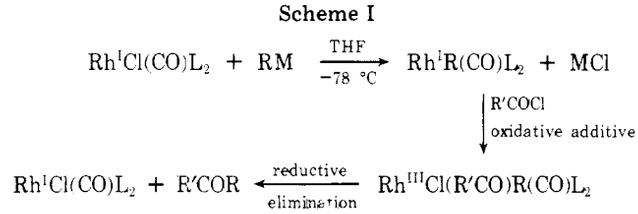
The classic reaction of acid chlorides with dialkylcadmium reagents provides an alternative, but little used, path which is limited by the cadmium reagent. The reaction of both organolithium and Grignard reagents with rhodium(I) halides is well established.[1-3] Similarly, the oxidative addition of acid chlorides to rhodium(I) complexes to give acyl rhodium(III) complexes is well known.[4-6] Therefore, it seemed likely to us

Table I. Synthesis of Ketones Using Polymer-Bound Rhodium Reagent Resin 1

No.	Organolithium reagent	Acid chloride	Registry no.	Ketone	Yield, %[a] Isolated	GLC
1	*n*-BuLi	C_6H_5COCl	98-88-4	C_6H_5COBu	61	>80
2	*n*-BuLi	*m*-NC-C_6H_4COCl	1711-11-1	*m*-NCC_6H_4COBu	60	>75
3	*n*-BuLi	$CH_3(CH_2)_{10}COCl$	112-16-3	$CH_3(CH_2)_{10}COBu$	58	>70
4	C_6H_5Li[c]	CH_3COCl	75-36-5	$CH_3COC_6H_5$	60	>60
5	C_6H_5Li	C_6H_5COCl		$C_6H_5COC_6H_5$	82	>90
6	C_6H_5Li	*m*-NCC_6H_4COCl		*m*-$NCC_6H_4COC_6H_5$	83	>90
7	C_6H_5Li	$CH_3OC(=O)-(CH_2)_4-COCl$	35444-44-1	$CH_3OC(=O)-(CH_2)_4-COC_6H_5$	56	
8	C_6H_5Li	*p*-H—C(=O)—C_6H_4—$COCl$	16173-52-7	*p*-H—C(=O)—C_6H_4COBu	32	
9	C_6H_5Li	$C_6H_5CH=CHCOCl$	102-92-1	$C_6H_5CH=CHCOC_6H_5$	42	
10	C_6H_5Li	c-C_3H_5COCl	4023-34-1	c-$C_3H_5COC_6H_5$	71	
11	C_6H_5Li		527-69-5		28	
12	C_6H_5Li	*p*-$NO_2C_6H_4COCl$[b]		No reaction[b]		
13	C_6H_5Li	*p*-$CH_3OC_6H_4COCl$[b]		No reaction[b]		
14	C_6H_5Li	$CH_3CH(CF_3)CH_2COCl$[b]		No reaction[b]		

[a] Yields are based on moles of acid chloride charged. [b] Corresponding carboxylic acid recovered in workup procedure. [c] Registry no., 591-51-5.

Scheme I



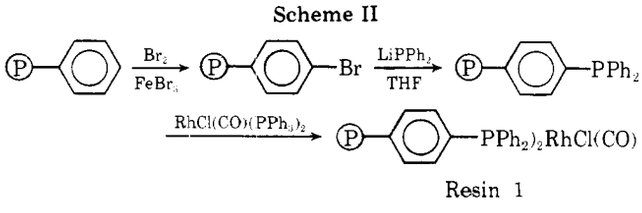
that these two reactions could be combined, as shown in Scheme I, to provide a ketone synthesis from organolithium (or Grignard) reagents and acid chlorides. The proposed reductive elimination step would produce the ketone and regenerate the starting rhodium complex.

This route proved satisfactory and initial studies, conducted independently, were reported in initial form by Hegedus et al.[7] and by us.[8] Since the work of Hegedus[7,9] was conducted using the soluble rhodium complex $RhCl(CO)(PPh_3)_2$, we decided to concentrate on the development of a polymer-attached rhodium derivative which should lead to the more convenient application of this complex in ketone synthesis. Interest in the use of polymeric reagents in organic synthesis has increased markedly in recent years.[10-12] Among the advantages offered by bound reagents are (1) easy purification of polymer-anchored intermediates from the reaction solvents and by-products and (2) easy recycling of the polymeric reagent if it is regenerated in the reaction. Since organorhodium derivatives are exceedingly expensive, these two advantages are significant considerations in any ketone synthesis via Scheme I.

Results and Discussion

A polymer-bound analogue of $RhCl(CO)(PPh_3)_2$ was prepared from styrene–divinylbenzene resins (Bio Rad S-Xl, 1% divinylbenzene, 14 000 mol wt exclusion limit) by Friedel–Crafts bromination followed by phosphination with lithium diphenylphosphide and thermal ligand exchange (Scheme II).[8] A single batch of resin 1 (see Experimental Section) was

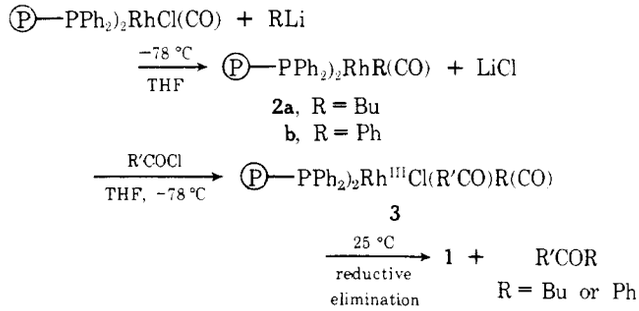
Scheme II



Resin 1

used throughout this study. Analysis showed 8.4% P and 5.3% Rh which corresponds to a P:Rh ratio of 5.3 and 60% of the phenyl rings in the resin substituted with diphenylphosphino groups. Thus, the resin contained a very high loading of phosphine groups making it very easy to replace all the triphenylphosphine groups with Ⓟ-PPh_2 moieties. Furthermore, since resin-anchored phosphine groups were present in such high density, leaching of rhodium from the polymer did not occur to a measureable extent during the course of this study.

Resin 1 proved to be a regeneratable solid-phase reagent for effecting the transformation of acid chlorides to ketones. When butyllithium or phenyllithium was added to a THF suspension of resin 1 at −78 °C, the corresponding butyl- or phenylrhodium derivative, **2**, was produced. After 2 h a slight



deficiency of the acid chloride in THF was added to the polymer suspension. The reaction mixture was held at −78 °C for several hours and then warmed to 25 °C. Reductive elimination from **3** occurred upon warming to give the product ketone, and resin **1** was regenerated. Thus, unsymmetrical ketones were generated under very mild conditions. Since the reagent was polymer anchored, it was simply separated from the product solution by filtration and washing. Eleven ketones were prepared as shown in Table I.

The synthesis of 1-(*m*-cyanophenyl)butanone is representative. Butyllithium (20 mmol in hexane) was added by syringe under nitrogen to a stirred THF suspension of resin 1 at −78 °C. The polymer had been preswollen in dry, degassed THF for 12 h under nitrogen and then cooled to −78 °C. Since swelling was rapid, a 30-min preswelling is more than sufficient. Best results were obtained by a very slow addition of butyllithium (from 30 min to 2 h). After an additional 20–35 min, *m*-cyanobenzoyl chloride (19.0 mmol) in 20 mL

of THF was added dropwise at −70 °C. The oxidative addition of the acid chloride and subsequent reductive elimination of the ketone took place at temperatures between −78 and −35 °C. The solvent was separated, by filtration, from the resin while the resin was simultaneously being washed with more cold, dry THF (−60 to −50 °C). Subsequent washings with THF and benzene were carried out and the combined organic layer was concentrated and distilled to give the 1-(*m*-cyanophenyl)butanone in 60% yield (11.4 mmol).

The intermediate arylrhodium derivatives are more stable than their alkyl counterparts, since metal hydride elimination cannot occur. In these cases the reactions were warmed to room temperature after acid chloride addition as recommended previously.[7,9]

The proposed alkyl- or arylrhodium(I) (i.e., **2**) and acylrhodium(III) (i.e., **3**) intermediates were not isolated but they have ample precedent in the literature.[13,14] Resin **1** exhibits a CO stretching frequency at 1984 cm^{-1} (broad in THF) which may be compared to a band at 1980 cm^{-1} for $RhCl(CO)(PPh_3)_2$.[7,9,15] This further characterizes the structure of the anchored rhodium derivative as that shown in Scheme II.

An important feature of this method is that functional groups which normally react with organolithium reagents may be carried through the procedure intact. For example, aldehyde, ester, and cyano functions, which are present in the acid chloride, remain unchanged in the product. Entries 6, 7, and 8 attest to this fact. For example, the monomethyl ester of adipoyl chloride produced the corresponding ketone in 56% yield (entry 7). The ester group was not attacked. The rapid formation of the alkyl (or acyl) rhodium(I) complex, **2**, removes the organolithium reagent from solution. Since complex **2** is not a highly nucleophilic reagent, it is inert to cyano, aldehydo, and ester functions at the conditions employed.

Several limitations accompany this path. First, secondary and tertiary alkyl rhodium intermediates undergo metal hydride elimination.[7,9] Thus, *tert*-butyllithium, isopropyllithium, and related organolithium reagents cannot be used effectively in this synthesis. A second limitation involves the failure of electron-deficient acid chlorides (e.g., *p*-nitrobenzoyl chloride) to undergo easy oxidative addition to alkyl (or aryl) rhodium intermediate **2**. The scope of these limitations has not yet been fully defined. When the rhodium complex is anchored to a resin (i.e., resin **1**) the same reagent can be cycled repeatedly. For example, one sample of resin **1** was reused in ten successive synthetic procedures to produce the entries 1–10 in Table I. After those ten reactions had been performed, a reaction identical with entry 1 was conducted again and a 57% yield of 1-phenylbutanone was obtained. Thus, no loss of activity was apparent.

Experimental Section

All solvents used were carefully dried and nitrogen saturated. THF and benzene were constantly refluxed over CaH_2 in a nitrogen atmosphere and distilled immediately before use. Acid chlorides or corresponding carboxylic acids were obtained commercially and either used as received or distilled immediately prior to use. The bromination and phosphination of the polystyrene–1% divinylbenzene resin (200–400 mesh)[16] has been previously described.

Preparation of a Polymer-Bound Analogue of $(PPh_3)_2RhCl(CO)$ (Resin 1.) Phosphinated resin (6 g, 8.8% P, 17.0 mmol P) and $(PPh_3)_2RhCl(CO)$ (4 g, 5.8 mmol) were placed in a nitrogen-purged flask, along with benzene (100 mL). The resulting slurry was stirred under nitrogen for 24 h at room temperature to accomplish ligand exchange. The resin was then recovered by filtration on a glass frit funnel and extracted with benzene under nitrogen in a Soxhlet extractor for 3 days to remove all soluble catalyst and ligand. The polymer-bound catalyst was then dried under vacuum (80 °C, 0.05 Torr) for 48 h. Analysis showed 8.4% P and 5.3% Rh, which corresponds to a P:Rh ratio of 5.3:1 and 61% of the polystyryl rings substituted with the diphenylphosphide moiety.

Rhodium-Mediated Ketone Synthesis. The synthesis of acetophenone is representative. To a dry, nitrogen-purged flask were charged 4.84 g of polymer-bound $RhCl(CO)(PPh_2)_2$ (resin **1**) (2.5 mmol Rh) and 100 mL of dry THF. The resulting slurry was stirred overnight under a nitrogen atmosphere to completely swell the resin. The flask was then cooled to −78 °C in a dry ice/acetone bath and phenyllithium [2.0 mmol in benzene/ether (70:30)] was added slowly by means of a syringe. The slurry was allowed to stir for an additional 2 h at −78 °C. At this time freshly distilled acetyl chloride (1.75 mmol in 10 mL of THF) was added by syringe. The slurry was maintained at −78 °C for an additional 4 h and then allowed to return slowly to room temperature. After stirring for 12 h at room temperature the slurry was filtered on a coarse glass frit funnel. The resin was then placed in 100 mL of fresh THF and stirred under nitrogen for 2 h. The slurry was again filtered and the recovered resin was stirred in dry benzene (100 mL) for 2 h. The resin was then recovered by filtration and vacuum dried (25 °C, 0.05 Torr). The THF filtrates were combined and solvent removed by evaporation. This residue was then dissolved in the benzene filtrate and LiCl removed by filtration. The benzene solution was then extracted with three portions of water (50 mL) and dried with $MgSO_4$ and benzene was removed by evaporation. The resulting residue was dissolved in 50 mL of ethyl ether and extracted with 50 mL of 3% aqueous NaOH solution. The ether layer was dried with $MgSO_4$ and ether removed by evaporation. Yield 0.126 g (1.05 mmol) of acetophenone, corresponding to a 60% yield based on acetyl chloride; mass spectrum shows parent ion at *m/e* 120; IR $\nu_{C=O}$ 1730 cm^{-1}; NMR δ 1.9 (s, 3 H, O=CCH_3), 7.2 (m, 5 H, phenyl).

Syntheses of other example ketones were carried out in a similar manner (yields quoted are after purification and based on acid chloride).

Cyclopropyl phenyl ketone was prepared from cyclopropylcarboxylic acid chloride (0.314 g, 3.0 mmol) and phenyllithium (3.5 mmol in 70:30 benzene/ether) in 71% yield by the above method. After dissolving in pentane, filtration, and evaporation of solvent, mass spectrum shows a parent ion at *m/e* 146; IR $\nu_{C=O}$ 1740 cm^{-1}; NMR δ 0.8–1.0 (d, 4 H, β-cyclopropyl), 1.28 (s, 1 H, α-cyclopropyl), 7.1–7.5 (m, 5 H, phenyl).

2-Benzoylfuran was prepared from 2-furoyl chloride (0.445 g, 3.5 mmol) and phenyllithium (3.78 mmol in 70:30 benzene/ether) in 28% yield. After dissolving in pentane, filtration, and evaporation of solvent, mass spectrum shows a fragmentation pattern with major peaks at *m/e* 77 and 67; IR $\nu_{C=O}$ 1730, $\nu_{C=C}$ 1570 cm^{-1}; NMR δ 7.0–7.6 (unresolved multiplet).

Methyl 5-oxodecanoate was prepared from monomethyladipoyl chloride (0.9 g, 5 mmol) and *n*-butyllithium (5 mmol in hexane) in 52% yield after vacuum distillation (160 °C, 2 mmHg): mass spectrum shows parent ion at *m/e* 200; IR $\nu_{C=O}$ (ester) 1730, $\nu_{C=O}$ 1710, $\nu_{C=O}$ 1230 cm^{-1}; NMR δ 0.9 (t, 3 H, CCH_3), 1.2–1.5 (m, 10 H, CCH_2C), 2.2 (d, 4 H, O=CCH_2), 3.5 (s, 3 H, O=$COCH_3$).

1,3-Diphenyl-2-propen-1-one was prepared from cinnamoyl chloride (0.625 g, 3.8 mmol) and phenyllithium (3.8 mmol in 70:30 benzene/ether) in 42% yield after recrystallization from pentane: mp 57–58 °C (lit.[17] 59 °C); mass spectrum shows parent ion at *m/e* 208; IR $\nu_{C=O}$ 1720, $\nu_{C=C}$ 1640 cm^{-1}; NMR δ 6.3 and 6.6 (q, 1 H, C=CH, J = 16 Hz), 7.7 and 8.0 (q, 1 H, C=CHC=O, J = 16 Hz), 7.4–7.6 (m, 10 H, phenyl).

5-Phenyl(4′-formyl)pentan-5-one was prepared from 4-formylbenzoyl chloride (0.8425 g, 5.0 mmol) and *n*-butyllithium (5.0 mmol in hexane) in 32% yield. After recrystallization from pentane: mp 134–136 °C; mass spectrum shows parent ion at *m/e* 190; IR $\nu_{C=O}$ 1680 cm^{-1}.

The other ketones listed in Table I gave IR, NMR, and mass spectra in accord with their structure and in properties were in agreement with the literature as indicated previously.[8,9]

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Registry No.—Cyclopropyl phenyl ketone, 3481-02-5; 2-benzoylfuran, 2689-59-0; methyl 5-oxodecanoate, 6093-95-4; 5-phenyl(4′-formyl)pentan-5-one, 61363-43-7; 1,3-diphenyl-2-propen-1-one, 94-41-7.

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(16) For a detailed description of the prewashing of styrene–divinylbenzene resin beads see J. M. J. Fréchet, *Polym. Prepr.*, **17**, 515 (1976).
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Selective Reductions. 22. Facile Reduction of α,β-Unsaturated Aldehydes and Ketones with 9-Borabicyclo[3.3.1]nonane. A Remarkably Convenient Procedure for the Selective Conversion of Conjugated Aldehydes and Ketones to the Corresponding Allylic Alcohols in the Presence of Other Functional Groups[1]

S. Krishnamurthy[2] and Herbert C. Brown*

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

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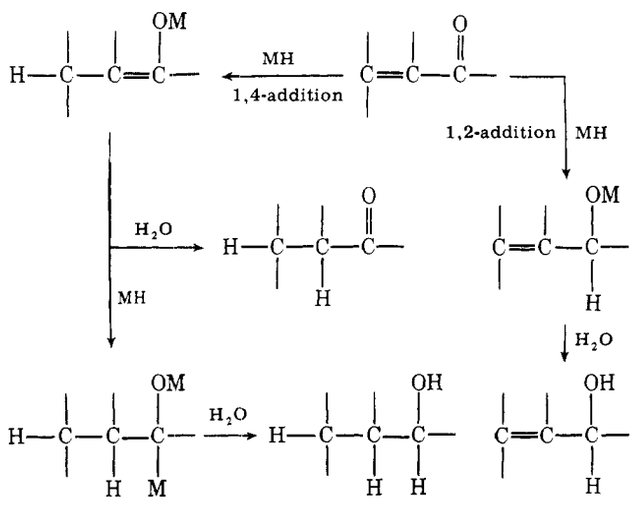
Conjugated aldehydes and ketones are reduced rapidly and quantitatively to the corresponding allylic alcohols by 9-borabicyclo[3.3.1]nonane in tetrahydrofuran in excellent purities. Even cyclic enones, such as 2-cyclohexenone and 2-cyclopentenone, are reduced cleanly to the desired allylic alcohols without concomitant attack at the double bond. The development of a unique workup procedure renders possible the isolation of carbinols in excellent yields. Unlike more conventional reagents, such as aluminum hydride and diisobutylaluminum hydride, the mildness of the reagent, 9-BBN, permits the presence of almost any other functional groups, such as ester, amide, carboxylic acid, nitro, halogen, nitrile, etc. The superior ability of this reagent for the selective reduction of α,β-unsaturated aldehydes and ketones was confirmed by the selective conversion of *o*-nitrocinnamaldehyde to *o*-nitrocinnamyl alcohol and of 4-carbethoxy-3-methyl-2-cyclohexenone to 4-carbethoxy-3-methyl-2-cyclohexenol in yields of 76 and 95%, respectively. The present development provides a highly convenient synthetic procedure for the selective reduction of conjugated aldehydes and ketones in a multifunctional molecule, where this is required in synthetic operations.

Selective reduction of α,β-unsaturated aldehydes and ketones to the corresponding allylic alcohols (1,2-addition) has been examined with a variety of hydride reducing agents.[3] Often this is accompanied with conjugate reduction (1,4-addition) to a varying extent, thereby affording saturated aldehyde or ketone, accompanied by subsequent reduction to yield saturated carbinol (Scheme I). Systematic exploration of the reaction of conjugated aldehydes and ketones with sodium borohydride, a mild reducing agent, clearly indicates that the reaction invariably yields substantial proportions of saturated carbinols[4] (1,4-addition). Comparatively, the results realized with lithium aluminum hydride, a powerful reducing agent, are considerably better. However, this can by no means be adapted as a general procedure; labile systems, such as 2-cyclopentenones, yield considerable amounts of the conjugate reduction products. Application of alkoxy derivatives of lithium aluminum hydride, such as lithium trimethoxyaluminohydride and lithium tri-*tert*-butoxyaluminohydride, do not improve the results. Sodium cyanoborohydride reduces acyclic conjugated aldehydes and ketones cleanly to the allylic alcohols; however, cyclic enones give a mixture of allylic and saturated alcohols.[5]

Scheme I



The failure to achieve clean reduction of α,β-unsaturated aldehydes and ketones with conventional reducing systems led to the exploration of various other new hydride reducing agents. The development of aluminum hydride as a reducing agent in our laboratory and its application to 2-cyclopentenone considerably decreased the unwanted 1,4-reduction products.[6] Recently, diisobutylaluminum hydride has been reported to reduce 2-en-1-ones to the corresponding allylic carbinols in higher yields and cleaner products than observed with aluminum hydride.[7] Unfortunately, its application to acyclic enones appears to give considerable amounts of the undesired saturated products.[3b] Moreover, both aluminum