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naphthol, 135-19-3; resorcinol, 108-46-3; allyl bromide, 590-14-7; 3-(allyloxy)phenol, 1616-51-9.

Supplementary Material Available: Relative reactivity studies of *trans*- and *cis*-1,2-dimethoxy-4-propenylbenzene with phenols using iodobenzene bis(trifluoroacetate) and NMR spectra of selected compounds (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Reductive Deoxygenation of Ketones and Secondary Alcohols by Organoaluminum Lewis Acids[1]

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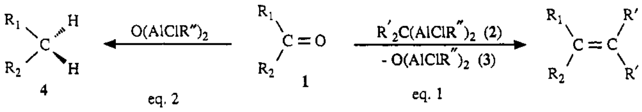
The reductive deoxygenation of ketones and secondary alcohols to the corresponding methylene hydrocarbons has been achieved in good to excellent yield by the combined action of an aluminum hydride source and a strongly Lewis-acidic aluminum reagent. Such reductions were successful with diaryl ketones, alkyl aryl ketones, and dialkyl ketones, as exemplified by the reduction of benzophenone, acetophenone and 5-nonanone, respectively. The corresponding secondary alcohols of these ketones, namely benzhydrol, 1-phenyl-1-ethanol, and 5-nonanol, could also be converted into their respective methylene hydrocarbons by Lewis-acidic sources of aluminum hydride. All such reductions of ketones could be conducted in a single reaction flask in a one-, two-, or three-step process. In the one-step process, which is most suitable for diaryl ketones, i-BuAlCl$_2$ may be employed as both the hydride source and the Lewis acid. For alkyl aryl ketones a two-step process, consisting first of reduction with i-Bu$_2$AlH and then treatment with AlBr$_3$ (with or without catalysis by Cp$_2$TiCl$_2$), leads to better yields. Finally, for dialkyl ketones a three-step process proved to be preferred, wherein a sequential treatment with i-Bu$_2$AlH, AlBr$_3$ and then additional i-Bu$_2$AlH (with a Ni(acac)$_2$ catalyst) gives the highest conversion to alkane. If required, residual alkene may be removed by a brief catalytic hydrogenation or treatment with BH$_3$·THF. The ease of deoxygenating the foregoing ketones and secondary alcohols appears to be governed by the ease of forming, and the relative stability of, the corresponding carbenium ion intermediates, namely Ar$_2$HC$^+$ > ArRHC$^+$ > R$_2$HC$^+$. The driving force for such deoxygenations by these aluminum reagents undoubtedly is the exothermic formation of the dialuminoxane system, R$_2$Al–O–AlR$_2$.

Introduction

During a recent study of the alkylenating action of geminal dialuminoalkanes (**2**) upon ketones (**1**),[2a] two of us[2b] made the serendipitous observation that the dialuminoxane byproduct **3** (**a**, R″ = Et; **b**, R″ = i-Bu) had been able to reduce a small portion of the ketone to the corresponding methylene derivative **4**, especially in those cases where diaryl or aryl alkyl ketones were employed (eq 2; R$_1$, R$_2$ = Ar or R$_1$ = Ar; R$_2$ = R). Although the reduction of ketones to secondary alcohols by aluminum alkyls or hydrides is rich in precedent,[3] this type of reductive deoxygenation is not. Only a limited study of the reducing action of combinations of LiAlH$_4$ and AlX$_3$ in diethyl ether has been made, in which alkyl aryl and diaryl ketones were shown to be similarly reduced in yields ranging between 20% and 90%.[4] However, the reduction of ketones to methylene derivatives has been achieved by a number of other reagents,[5] prominent among which are zinc with acid as in the Clemmensen reduction,[6a] sodium borohydride with trifluoroacetic acid, as found by Gribble and co-workers,[6b] and hydrazine with base as in the Wolff–Kishner reduction.[7] Unfortunately, the most versatile of these reduction methods necessitate the use of strongly acidic or basic reagents with polar solvents, and such conditions can lead to undesired side reactions. The great advantage that aluminum reagents like **3** would offer for such reductive deoxygenations is that they can react in hydrocarbon media and the methylene derivative can be isolated from the aluminoxane byproduct without hy-



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(1) Part 49 of the series Organometallic Compounds of Group III. Part 48: Eisch, J. J.; Liu, Z.-R.; Singh, M. *J. Org. Chem.*, in press.

(2) (a) Piotrowski, A. M.; Malpass, D. B.; Boleslawski, M. P.; Eisch, J. J. *J. Org. Chem.* **1988**, *53*, 2829 (b) Eisch, J. J.; Boleslawski, M. P., unpublished studies, 1987.

(3) Bruno, G. *The Use of Aluminum Alkyls in Organic Synthesis*; Ethyl Corporation: Baton Rouge, LA, original edition, 1968, and Supplements 1969–1972 and 1973–1978.

(4) Hystrum, R. F.; Berger, C. R. A. *J. Am. Chem. Soc.* **1958**, *80*, 2896.

(5) Other reagents effecting the conversion R$_2$CO → R$_2$CH$_2$ are (a) Li in liquid ammonia (Hall, S. S.; Lipsky, S. D.; McEnroe, F. J.; Bartels, A. P. *J. Org. Chem.* **1971**, *36*, 2588). (b) Raney Ni in ethanol (Mitchell, R. H.; Lai, Y.-H. *Tetrahedron Lett.* **1980**, *21*, 2637). (c) 10% Pd on charcoal with H$_2$ (Brieger, G.; Fu, T.-H. *J. Chem. Soc., Chem. Commun.* **1976**, 757). (d) Cp$_2$TiCl$_2$ and Na (van Tamelen, E. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 5290). (e) Et$_3$SiH with acid (West, C. T.; Donnelly, S. J.; Kooistra, D. A.; Doyle, M. J. *J. Org. Chem.* **1973**, *38*, 2675). (f) PhSeH and Ph$_3$SnH (Seebach, D.; Beck, A. K. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 806).

(6) (a) Martin, E. L. In *Organic Reactions*; Adams, R. Ed.; John Wiley & Sons: New York, 1942; Vol. I, p 155. (b) Gribble, G. W.; Kelly, W. J.; Emery, S. E. *Synthesis* **1978**, 763.

(7) Todd, D. In *Organic reactions*; Adams, R., Ed.; John Wiley & Sons: New York, 1948; Vol. II, p 378.

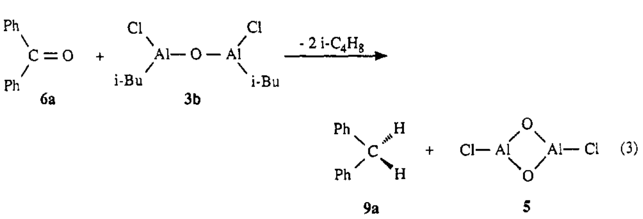
0022-3263/92/1957-2143$03.00/0

Table I. Reductive Deoxygenation of Benzophenone by Organoaluminum Lewis Acids

entry	reagents (steps)[a]	temperature, °C (time, h)	product (% yield)[b]
1	i-Bu_2AlH	90 (6)	Ph_2CHOH (95)
2	(i-BuClAl)$_2$O	110 (12)	Ph_2CH_2 (70)[c]
3	i-$BuAlCl_2$	90 (20)	Ph_2CH_2 (79) $Ph_2C{=}CHCHMe_2$ (8)
4	i-Bu_2AlH i-$BuAlCl_2$ (2)	90 (6) 90 (20)	Ph_2CH_2 (87)
5	i-Bu_2AlH $AlBr_3$ (2)	90 (6) 90 (15)	Ph_2CH_2 (95)
6	i-$BuAlCl_2$[d]	90 (20)	Ph_2CH_2 (56) $Ph_2C{=}CHCHMe_2$ (25)

[a] Where two aluminum reagents were employed, they were added to the heptane solution of the ketone in steps and allowed to react for the stated time. [b] The yields of products are for the isolated organic compounds obtained upon hydrolysis and have not been optimized. [c] Friedel–Crafts alkylation products of the toluene solvent by the Ph_2CH^+ fragment were also formed. [d] In this reaction, 5 molar percent of anhydrous nickel(II) acetylacetonate was added.

drolysis (eq 3), since the oxygen eliminated is tied up in an aluminoxane oligomer (e.g., **5**)[8]



In attempting to understand this unprecedented reducing action of neutral aluminum alkyls, we conjectured that the heightened Lewis acidity of the dialuminoxane might be determinant in rupturing the C–O bond in such ketones.

With the hypothesis that an effective reducing agent would require the presence of an Al–H bond[9a] and a highly Lewis-acidic center, we have now examined a series of isobutylaluminum derivatives containing Al–O or Al–X bonds for heightened Lewis acidity and have identified reagents and experimental conditions for reductively deoxygenating diaryl, aryl alkyl, and dialkyl ketones in very good to excellent yield. As typical ketonic substrates we have employed benzophenone (**6a**), acetophenone (**6b**), and 5-nonanone (**6c**).[9b]

Results

To verify that dialuminoxanes can reduce ketones to their methylene derivatives, bis(chloroisobutyl)dialuminoxane (**3b**) was prepared by the controlled hydrolysis of diisobutylaluminum chloride.[10] Heating benzophenone (**6a**) with **3b** in refluxing toluene led to a 70% conversion to diphenylmethane (**9a**, eq 3). The balance of the product consisted of the secondary alcohol **8a** and Friedel–Crafts alkylation products of the toluene by the diphenylmethyl cation. The last-mentioned products could be avoided by conducting subsequent reductions in heptane or methylcyclohexane.

Table II. Reductive Deoxygenation of Acetophenone by Organoaluminum Lewis Acids

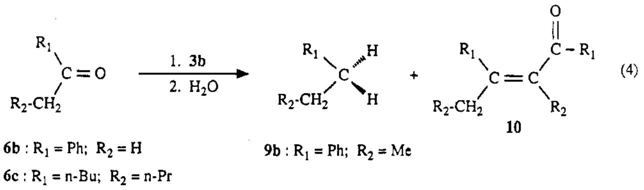
entry	reagents (steps)[a]	temperature, °C (time, h)	product (% yield)[b]
1	i-Bu_2AlH	90 (6)	$PhCH(OH)CH_3$ (90)
2	(i-BuClAl)$_2$O	110 (12)	$PhCH_2CH_3$ (15) $PhMeC{=}CHC(O)Ph$ (55)[c]
3	i-$BuAlCl_2$	90 (20)	$PhCH_2CH_3$ (20) $PhMeC{=}CHC(O)Ph$ (65)
4	i-Bu_2AlH $AlBr_3$ (2)	90 (6) 90 (20)	$PhCH_2CH_3$ (65)
5	i-Bu_2AlH $AlBr_3$[d] (2)	90 (6) 90 (20)	$PhCH_2CH_3$ (75)

[a] Cf. footnote *a*, Table I. [b] Cf. footnote *b*, Table I. [c] Friedel–Crafts alkylation of the toluene solvent by the

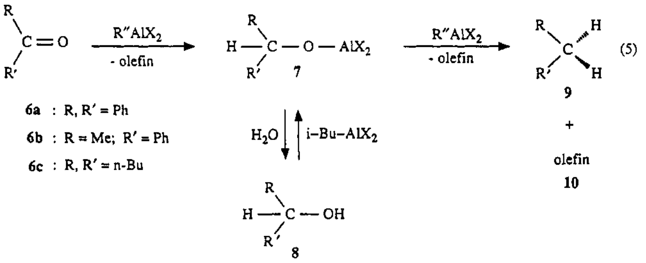
$$Ph\overset{+}{C}HCH_3$$

fragment was also observed. [d] In the second step, the addition of $AlBr_3$, 5 molar percent of titanocene dichloride was also added.

Attempts to employ dialuminoxane reagents **3b** to deoxygenate aryl alkyl ketone **6b** or dialkyl ketone **6c** were largely unsuccessful: **6b** yielded a modest amount of methylene derivative (**9b**) and mostly the aldol condensation product **10** (eq 4). The outcome with dialkyl ketone **6c** was even more discouraging: essentially only reduction to the alcohol and aldol condensation products like **10** were observed. Even an attempt to replace dialuminoxane **3b** with i-$BuAlCl_2$ gave a similar outcome: it reduced benzophenone to diphenylmethane in high yield (with a small amount of alkylation byproduct) but caused little or no conversion of acetophenone or 5-nonanone into their methylene derivatives. Again in these cases, enolate salt formation and aldol condensation were the preponderant reactions (Table I).



Since these reductions involve the aluminum alkoxide of the secondary alcohol as an intermediate (**7**, eq 5), it is logical to expect that the secondary alcohols themselves (**8**) could be reduced to the hydrocarbon by treating them with the same R″–AlX_2 reagents (X = halide, or R_2Al–O).



Because of the difficulties encountered in reducing enolizable ketones (**6b** and **6c**), it was then decided to proceed stepwise by reducing **6** to **7** with i-Bu_2AlH before increasing the Lewis acidity by adding AlX_3. By employing this two-step process, there would be no enolizable ketone available to react with the strong Lewis acid. In fact, this two-step process of first adding i-Bu_2AlH to yield **7** and then $AlBr_3$ to increase the Lewis acidity did effect the

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[8] Structure **5**, representing an aluminoxane dimer, is only exemplary of the wide variety of oligomers possibly formed.

[9] (a) An Al–H bond either was initially present in the organoaluminum reagents employed or was potentially available from an CH_3CH_2–Al or $(CH_3)_2CHCH_2$–Al group by the thermal elimination of olefin (cf. ref 14). (b) Although an extensive survey of the compatibility of various substituents on ketones with such reducing agents has not been carried out, it is already clear that reduced substituents, such as R, R_2N, and some X groups, may be inert, that R–O and R–S groups will be dealkylated but O–Ar and S–Ar bonds remain intact and that oxidized groups, such as R–CO, R–SO_2, NO_2, and CF_3, will be reduced.

[10] Boleslawski, M. P. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1986; Vol. III, p 472.

Table III. Reductive Deoxygenation of 5-Nonanone by Organoaluminum Lewis Acids

entry	reagents (steps)[a]	temperature °C (time, h)	product (% yield)[b]
1	i-Bu_2AlH	90 (6)	*n*-Bu_2CHOH (95)
2	i-Bu_2AlH	90 (24)	*n*-Bu_2CHOH (93)
	i-$BuAlCl_2$ (1)		
3	i-Bu_2AlH + i-$BuAlCl_2$	90 (8)	*n*-Bu_2CHOH (60)
	$AlCl_3$ (2)	90 (24)	nonenes (30)
			n-nonane (5)
4	i-Bu_2AlH^c		nonenes (70)
	$AlBr_3$ (2)	90 (20)	*n*-nonane (15)[e]
5	i-Bu_2AlH	90 (6)	nonenes (32)[e]
	$AlBr_3$	90 (20)	*n*-nonane (48)
	i-Bu_2AlH^d (3)	90 (6)	

[a] Cf. footnote *a*, Table I. [b] Cf. footnote *b*, Table I. [c] In the first step, 5 molar percent of zirconocene dichloride was also added. [d] In the third step, namely the addition of a further 1.1 molar equivalents of i-Bu_2AlH, 5 molar percent of nickel(II) acetylacetonate was also added. [e] Small amounts of isobutylated nonenes and nonene dimers (15%) were also formed but *n*-nonane and nonenes could be readily separated from them by gas chromatography or by fractional distillation.

Table IV. Reductive Deoxygenation of Various Hydroxy Organic Compounds, ROH

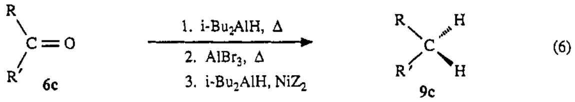
R	reagents (steps)[a]	temperature, °C (time, h)	product (% yield)[b]
Ph_2CH	i-Bu_3Al	20 (1)	Ph_2CH_2 (80)
	$AlBr_3{}^c$ (2)	100 (24)	
PhMeCH	i-Bu_3Al	20 (1)	$PhCH_2CH_3$ (75)
	$AlBr_3{}^c$ (2)	100 (24)	
n-Bu_2CH	i-Bu_3Al	20 (1)	nonenes (75)
	$AlBr_3{}^d$ (2)	100 (24)	*n*-nonane (10)
n-Bu_2CH	i-Bu_3Al	20 (1)	nonenes (35)[f]
	$AlBr_3{}^d$	100 (12)	*n*-nonane (50)
	i-Bu_2AlH^e (3)	100 (6)	
n-C_9H_{19}	i-Bu_3Al	20 (1)	no reduction
	$AlBr_3$ (2)	100 (24)	
p-MeC_6H_4	i-Bu_3Al	20 (1)	no reduction
	$AlBr_3$ (2)	100 (24)	

[a] A solution of the hydroxy substrate in heptane was treated with i-Bu_3Al at 20 °C; isobutane evolution signaled the formation of ROAl-i-Bu_2. [b] Cf. footnote *b*, Table I. [c] Five molar percent of titanocene dichloride was added with the $AlBr_3$. [d] Five molar percent of zirconocene dichloride was added with the $AlBr_3$. [e] Five molar percent of nickel(II) acetylacetonate were added with the further 1.1 molar equiv of i-Bu_2AlH. [f] Cf. footnote *e*, Table III.

conversion of acetophenone into ethylbenzene in very satisfactory yields. Such yields could be further improved by adding titanocene dichloride as a hydrometallating catalyst (Table II).

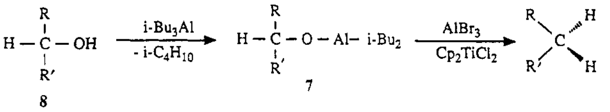
With dialkyl ketone **6c**, however, this two-step process resulted in deoxygenation but gave in good yield a mixture of principally the corresponding olefin(s) containing about 10% of nonane (Table III). In practice, this product can be subjected to a mild catalytic hydrogenation or to treatment with BH_3·THF to complete the conversion to alkane **9c**.[11] Nevertheless, in the hope of achieving this reduction as a third step in the same reaction flask, the unhydrolyzed reaction products of the two-step process were treated with another equivalent of i-Bu_2AlH. Although heating and subsequent hydrolysis increased the proportion of nonane (10–20%), dimers of the nonenes and isobutylated nonenes also were produced.

To enhance the reducing action of the i-Bu_2AlH in this third step, various hydroalumination promoters were evaluated, such as titanocene dichloride,[12] zirconocene dichloride,[12] and nickel(II) acetylacetonate.[13,14] Although the titanium promoter was wealky effectual and the zirconium agent moderately effective, the addition of the nickel salts in the third step led, upon subsequent hydrolysis, to a considerable conversion to nonane (60%, Table III). Thus, the transformation of dialkyl ketones to their methylene derivatives in one process involves three steps of adding sequentially i-Bu_2AlH, $AlBr_3$, and finally i-Bu_2AlH with $Ni(acac)_2$ (eq 6).[15a] The remaining nonenes in this product can be converted into *n*-nonane by a subsequent catalytic hydrogenation[11a] or by treatment with BH_3·THF and an acetolytic workup.[11b]



(6)

The aforementioned one-, two-, and three-step processes for the reduction of ketones (eqs 3, 5, and 6) were found to be readily adaptable to the corresponding secondary alcohols, benzhydrol (**8a**), 1-phenyl-1-ethanol (**8b**), and 5-nonanol (**8c**). Such alcohols were simply treated with i-Bu_3Al to produce the diisobutylaluminum alkoxide **7** (X = i-Bu). In the cases of diarylmethanol **8a** and alkylarylmethanol **8b**, this aluminum alkoxide was then heated with $AlBr_3$, advantageously in the presence of titanocene dichloride (eq 7). With dialkylmethanol **8c**, the heating step with $AlBr_3$ was followed by a third step involving heating with an equivalent of i-Bu_2AlH and the $Ni(acac)_2$ promoter. The results of such reductions are given in Table IV.



(7)

Although the reduction of such secondary alcohols by this procedure proceeded smoothly and in satisfactory overall yields, the attempted reductions of primary alcohols and phenols, such as 1-nonanol and *p*-cresol, led to no conversion at all.

Discussion

The unsuccessful attempts to deoxygenate primary alcohols and phenols, as well as the successful reductions of ketones and secondary alcohols, by these organoaluminum Lewis acids can be understood in terms of a rate-determining heterolytic rupture of the final C–O bond in the aluminum alkoxide intermediate (**7**). The observed decreasing ease of deoxygenation, $Ph_2C{=}O$ > $PhMeC{=}O$ > *n*-$Bu_2C{=}O$ and $Ph_2HC{-}OH$ > $PhMeHC{-}OH$ > *n*-$Bu_2HC{-}OH$, is consistent with the development of carbenium ion character in the transition state **11**. Such a view would account for the necessity of a strong Lewis acid

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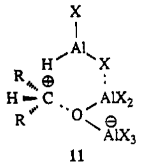
[11] (a) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, 1972; pp 1–34. (b) Knights, E. F.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 5280, 5281.

[12] It has been widely recognized for at least 25 years that titanium(IV) and zirconium(IV) compounds catalyze the transfer of AlH_3 from i-Bu_3Al to isomeric olefin mixtures to yield principally the 1-alkylaluminum product (Asinger, F.; Fell, B.; Janssen, R. *Chem. Ber.* **1964**, *97*, 2515). Thus the claim published in 1976 that the Japanese authors had discovered that transition metal halides (Ti and Zr) catalyze the addition of $LiAlH_4$ and AlH_3 to olefins must be judged as spurious (Sato, F.; Sato, S.; Sato, M. *J. Organomet. Chem.* **1976**, *122*, C25; **1977**, *131*, C26).

[13] Eisch, J. J.; Foxton, M. W. *J. Organomet. Chem.* **1968**, *12*, P33.

[14] The elimination of isobutylene from triisobutylaluminum has long been known to be catalyzed by nickel salts: Lehmkuhl, H.; Ziegler, K.; Gellert, H.-G. In *Methoden der Organischen Chemie*; Müller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1970; Vol. XIII-4, p 41.

[15] Eisch, J. J.; Zheng, G.-X., work in progress. (a) The nonenes and *n*-nonane formed by such a three-step reduction (80%) are accompanied by about 15% of a mixture of isobutylated nonene ($C_{13}H_{25}$) and nonene dimers ($C_{18}H_{36}$). (b) The chemical behavior of 1,3-butanediol and of the *o*-, *m*-, and *p*-hydroxybenzyl alcohols in such reduction processes is currently being evaluated.



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in such reductions and for the failure of primary alcohols and phenols to undergo reduction (their respective carbenium ions would be much less stable). This differing ease of reducibility may be used to advantage for the selective removal of tertiary or secondary hydroxyl groups from diols containing primary hydroxyls as well, such as in 1,3-butanediol, or in the selective deoxygenation of aromatic compounds containing both benzylic and phenolic hydroxyl groups.[15b]

Finally, some comment on the transition-metal catalysis employed in these reductions is in order. Small amounts of titanocene dichloride or zirconocene dichloride improved the conversion of both the diaryl ketone (**6a**) and the alkyl aryl ketone (**6b**) to the final methylene derivative, as in the one-step and the two-step process. Titanium and zirconium compounds are known to form hydrides which catalyze hydroaluminations[12] and hydromagnesiations.[16] On the other hand, the same transition metal promoters proved to be only of modest activity in promoting hydroalumination in the three-step process for reducing dialkyl ketone **6c** to the alkane. In this instance, hydroalumination was effectively promoted by nickel(II) acetylacetonate. Nickel salts are known to be promptly reduced to nickel(0) by aluminum alkyls,[17] and the resulting nickel(0) is the actual, highly active catalyst for the hydroalumination of acetylenes[13] and olefins.[18]

In light of nickel's established catalytic activity in hydroalumination, it was surprising[19] to observe that small amounts of Ni(acac)$_2$ did not promote the reducing action of i-BuAlCl$_2$ in the one-step reduction of benzophenone to diphenylmethane, but rather promoted the carbalumination of **6c** to yield 3-methyl-1,1-diphenyl-1-butene (**12**, eq 8). This result would seem to require the intermediacy of an isobutylnickel derivative at a reaction temperature of 90 °C. Such an indication is astonishing, since dialkylnickel derivatives that are not stabilized by R$_3$P or R$_3$N ligands are known to decompose readily at −100 °C.[19] The nature of this catalyzed carboalumination is under active study.[15]

$$\underset{\textbf{6a}}{\mathrm{Ph_2C{=}O}} \xrightarrow[\text{2. } \mathrm{H_2O}]{\text{1. i-BuAlCl}_2\text{, NiZ}_2} \underset{\textbf{9a}}{\mathrm{Ph_2CH_2}} + \underset{\textbf{12}}{\mathrm{Ph_2CH{=}CH{-}CHMe_2}} \quad (8)$$

Experimental Section

Instrumentation and Analyses. All melting points were measured with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded on Perkin-Elmer spectrophotometers, Models 457 and 283B, which were equipped with sodium chloride optics. Proton magnetic resonance spectra (^{1}H NMR) were obtained with a Varian spectrometer, Model EM-360, on pure samples or on 10% solutions in pure deuteriated solvents. The ^{1}H NMR data were reported on the δ scale in parts per million with reference to internal tetramethylsilane. Mass spectral data (MS) were collected with a Hewlett-Packard gas chromatograph–mass spectrometer, Model 5882B.

Gas–liquid phase chromatographic analyses (GC) were carried out with an F&M temperature-programmed chromatograph, Model 720, equipped with dual 12-ft columns of a 10% UC-298 phase on a Chromosorb W support and with an electronic peak-area integrator. Thin-layer chromatographic analyses (TLC) were done on Eastman Chromagram Sheets, no. 13181, consisting of silica gel with fluorescent indicator.

General Procedures. All steps in the preparation, transfer, and main reactions of the organometallic reagents studied here were conducted under an atmosphere of anhydrous and oxygen-free argon. All solvents and apparatus were likewise freed of traces of dissolved or adsorbed moisture and oxygen and then maintained under argon. Methods and techniques for working under anhydrous and anaerobic conditions have been described previously.[20]

Starting Materials and Products. Diisobutylaluminum hydride, isobutylaluminum dichloride, and triisobutylaluminum were obtained as neat reagents from Texas Alkyls Inc., Deer Park, TX. Anhydrous aluminum bromide and aluminum chloride, as well as titanocene dichloride and zirconocene dichloride, were purchased from Aldrich Chemical Co.

Benzophenone, acetophenone, and 5-nonanone were commercially available, as were the reduction products, diphenylmethane, ethylbenzene, and nonane. The secondary alcohols, benzhydrol, 1-phenyl-1-ethanol, 5-nonanol, and 1-nonanol, could be purchased or prepared in essentially quantitative yield by reducing the corresponding carbonyl derivative by one equivalent of i-Bu$_2$AlH in heptane at 80 °C. Other intermediate reduction products, such as the isomeric nonenes, were identified by combined GC–MS, IR, and ^{1}H NMR analyses by comparison with 1-, 2-, 3-, and 4-nonenes (trans) available from Aldrich Chemical Co. All the other hydrocarbon and secondary alcohols were similarly characterized.

Illustrative Experimental Procedures. One-Step Reduction of Benzophenone (6a) to Diphenylmethane (9a). A solution of 1.0 mmol of **6a** and 2.2 mmol of i-BuAlCl$_2$ in 25 mL of anhydrous heptane, maintained under a nitrogen atmosphere, was heated at reflux for 20 h, cooled to 25 °C, and then cautiously hydrolyzed with water. (**Warning**: These hydrolyses are markedly exothermic and are accompanied by gas evolution. The water should be introduced slowly (via a syringe or diluted with ether) into a well-stirred reaction mixture, which is cooled in an ice bath). Separation of the organic layer, drying over solid MgSO$_4$, solvent removal, and fractional distillation yielded 79% of diphenylmethane. The distillation residue was principally 3-methyl-1,1-diphenyl-1-butene (8%).

Two-Step Reduction of Acetophenone (6b) to Ethylbenzene (9b). On the same scale as the foregoing, **6b** was heated in heptane with 1.1 molar equiv. of i-Bu$_2$AlH at 70 °C for 4 h (withdrawal and hydrolysis of an aliquot showed by GC analysis complete conversion to MePhCHOH). Then 1.1 molar equiv of finely powdered, anhydrous AlBr$_3$ and 5 molar percent of titanocene dichloride were introduced. Heating at 90 °C was continued for 22 h, whereupon a *cautiously conducted* hydrolytic workup (cf. vida supra) was carried out. Fractional distillation of the organic residue, after drying the ethereal layer and solvent removal, gave a 75% yield of ethylbenzene.

Three-Step Reduction of 5-Nonanone (6c) to Nonenes and Nonane (9c). On the same scale as the foregoing, ketone **6c** was heated at 80 °C in heptane with 1.1 molar equiv of i-Bu$_2$AlH for 4 h (hydrolytic verification of complete conversion to *n*-Bu$_2$CHOH). Then 1.1 molar equiv of powdered AlBr$_3$ was added, and heating at reflux continued for 12 h. Finally, after cooling the reaction mixture was treated with 1.1 molar equiv of i-Bu$_2$AlH and 0.02 molar equiv of Ni(acac)$_2$. Further heating for 6 h and hydrolytic workup led to an 80% combined yield of nonenes and *n*-nonane upon fractional distillation (40:60).

Conversions of Secondary Alcohols into Diisobutylaluminum Alkoxides with Triisobutylaluminum and Subsequent Deoxygenation. Preparatory to reducing secondary alcohols, benzhydrol (**8a**), 1-phenyl-1-ethanol (**8b**), and 5-nonanol (**8c**), these compounds were converted into their diisobutylaluminum alkoxides. To 1.1–11.0 mmol of triisobutylaluminum

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dissolved in heptane at 20 °C was added dropwise a heptane solution of 1.0–10.0 mmol of the alcohol (equimolar with the i-Bu_3Al). The solution was stirred for 1 h, during which time the isobutane gas was evolved.

The resulting solution was treated in two ways: (1) with the alkoxides of **8a** and **8b**, it was heated with 1.1 molar equiv of $AlBr_3$ and 0.05 equiv of Cp_2TiCl_2 for 24 h and worked up as with the ketone reductions and (2) with the alkoxide of **8c**, it was subjected successively to 1.1 mmol of $AlBr_3$ at reflux for 12 h and to 1.1 mmol of i-Bu_2AlH and 0.02 molar equiv of $Ni(acac)_2$ for 6 h, followed by the usual workup.

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Registry No. **3b**, 45095-66-7; **6a**, 119-61-9; **6b**, 98-86-2; **6c**, 502-56-7; **8a**, 91-01-0; **8b**, 98-85-1; **8c**, 623-93-8; **9a**, 101-81-5; **9b**, 100-41-4; **9c**, 111-84-2; **10b**, 495-45-4; **12**, 35467-39-1; *i*-Bu_2AlH, 1191-15-7; *i*-$BuAlCl_2$, 1888-87-5; $AlBr_3$, 7727-15-3; $C_9H_{19}OH$, 143-08-8; *p*-MeC_6H_4OH, 106-44-5; *i*-Bu_3Al, 100-99-2; nonene, 27215-95-8; nickel(II) acetylacetonate, 3264-82-2; titanocene dichloride, 1271-19-8.

Alkyne Reactions with the Cyclopalladated 8-Methylquinoline Ligand: Synthesis of Novel Heterocyclic Compounds with a Bridgehead Nitrogen[1]

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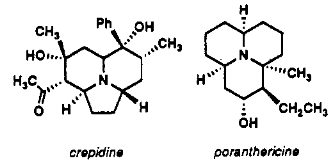
The stepwise reaction of cyclopalladated 8-methylquinoline (compound 1, obtained via intramolecular metalation of 8-methylquinoline by Pd(II)) with 2 equiv of various internal alkynes affords 4*H*-indolo[2,1,7-*cde*]quinolizines 3 through simultaneous Pd-mediated C–C and C–N bond formation. This reaction displays a high selectivity provided that the first alkyne reacting with 1 bears two electron-withdrawing substituents such as $-CF_3$ or $-CO_2Me$ and that the second alkyne is also substituted by electrophilic substituents. Varying the reaction conditions allowed us to isolate organometallic intermediates, whose nature shed some light upon the mechanism of the formation of 3. Several deviations from the synthesis of 3 were encountered when different alkynes were reacted with 1, e.g., with ethyl-3-phenylpropynoate a four-substituted α-pyrone was synthesized through C–O activation of one of the ester functions.

Introduction

The indolizine (pyrrolo[1,2-*a*]pyridine) and quinolizine (pyrido[1,2-*a*]pyridine) nuclei are present in a large number of alkaloids. These bicyclic ring systems have been extensively studied not only for their use as drugs[2] but also by virtue of their applications in photographic processes[3] and as dyestuffs.[4] Naturally occurring derivatives include perhydroindolizine (indolizidine) and octahydroquinolizine (quinolizidine), trivially known as the alkaloids δ-coniceine and norlupinane, respectively. These fragments have been observed in several biologically active alkaloids such as (the

Chart I



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