Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PRELIMINARY COMMUNICATION

NICKEL-CATALYZED HYDRALUMINATION OF ALKYNES AND THE NICKEL EFFECT IN THE ZIEGLER DIMERIZATION OF ETHYLENE

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(Received February 13th, 1968)

Interest in the hydralumination of alkynes recently has been quickened by the findings that suitable treatment of the resulting vinylaluminum compounds can lead either to *cis*-[1-3] or *trans*-[4-6] alkenes, as well as to unsaturated alcohols[6] and carboxylic acids[3,6]. Although complexes of lithium hydride with alkylaluminum hydride[6] or with aluminum hydride[4,5] effect principally *trans*-hydralumination, dialkylaluminum hydrides normally achieve an exclusively *cis*-hydralumination of alkynes[1,2]*. However, in certain cases hydralumination with dialkylaluminum hydrides may require heating at 50–60° for reasonable rates and under these conditions inevitable isomerization to the *trans*-adduct of the alkyne[2] and reductive dimerization of alkyne to an alkadienylaluminum system[1,2] may interfere. We now wish to report that small amounts of nickel salts markedly accelerate the rate of *cis*-hydralumination of alkynes. The amounts of concurrent *trans*-hydralumination and dimerization usually are modest. Besides the preparative advantage of such a catalyzed hydralumination, these observations have a significant bearing on the mechanism of the Ziegler process for the catalytic dimerization of ethylene[7].

To exhibit the catalytic effect of nickel salts, reaction pairs of the individual alkynes dissolved in hexane or heptane, one solution containing 1.6 molar percent of anhydrous nickel acetylacetonate (relative to the alkyne), were treated each with one equivalent of diisobutylaluminum hydride. The extents of hydralumination for both the catalyzed and the uncatalyzed reactions, as well as the *cis*–*trans* ratios for the catalyzed hydralumination under kinetic control and under further heating, are compiled in Table 1. The alkynes studied, 4-octyne, 1-phenylpropyne and diphenylacetylene, were chosen to embrace various types of internal alkynes; phenylethynyltrimethylsilane was examined, since its uncatalyzed hydralumination unexpectedly gave the *trans*-adduct[5]. In addition, the orientation in the catalyzed *cis*-hydralumination of 1-phenylpropyne was of interest. By deuterium oxide treatment the ratio of $C_6H_5C(AlR_2)$=$CHCH_3$/ C_6H_5CH=$C(AlR_2)CH_3$ was found to be 2/1; in the uncatalyzed reaction the ratio is 4.6/1.

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*With certain trialkylsilyl- or trialkylgermyl-alkynes dialkylaluminum hydrides can lead almost exclusively to *cis*- or *trans*-hydralumination, depending whether or not a tertiary amine is present; *cf.* ref. 5

TABLE 1

NICKEL-CATALYZED HYDRALUMINATION OF ALKYNES

Alkyne	Conversion (%, h),25°[a]		*Cis–trans* ratio	
	nickel-catalyzed	uncatalyzed	50% reaction nickel-catalyzed 25°	completed reaction nickel-catalyzed (°C, h)
$n\text{-}C_3H_7C{\equiv}C\text{-}n\text{-}C_3H_7$	50,0.25 100, 2	50,24.0	all *cis*[b]	all *cis*,60°,24
$CH_3C{\equiv}CC_6H_5$	50,0.50 100,3	14,24.0	97/3[b,c]	94/6,25°,24 30/7[d],60°,65
$C_6H_5C{\equiv}CC_6H_5$	50,1.0 100,4	26,72.0	78/22[b,e]	12/88,60°,20
$(CH_3)_3SiC{\equiv}CC_6H_5$	50,2[f]	50,2	15/85[g]	7/93,0°,20

[a] General reaction conditions: 5.6 mmoles $(iso\text{-}C_4H_9)_2AlH$ added to 5.6 mmoles alkyne and, for the nickel-catalyzed reactions, 1.6 molar % anhydrous nickel acetylacetonate mixed with 10 ml hexane or heptane (20 ml in case of diphenylacetylene). Reactions stirred at 25 ± 5° (except for the silylacetylene) and samples withdrawn, hydrolyzed and submitted to GLC analysis on 10% silicon oil-on-firebrick columns. [b] Uncatalyzed hydralumination gives only *cis*-alkene upon hydrolysis. [c] By deuterium oxide treatment and NMR analysis, *cis*-aluminum compounds were shown to be a 2/1 mixture of $C_6H_5C(AlR_2){=}CHCH_3$ and $C_6H_5CH{=}C(AlR_2)CH_3$. [d] Hydrolysate contains 30% n-propylbenzene. [e] As determined by sampling, this ratio is invariant (± 2%) from moment of mixing until almost complete reaction. [f] Reaction was conducted at 0°. [g] After 20 min 20% had reacted and *cis–trans* ratio was 25/75; uncatalyzed hydralumination gives 99% *trans*- alkene upon hydrolysis.

Examination of the foregoing results shows that the principally *cis*-hydralumination of internal alkynes is strongly catalyzed by nickel salts. Furthermore, it is noteworthy that the principally *trans*-hydralumination of phenylethynyltrimethylsilane is insensitive, in gross rate, to nickel catalysis. However, the isomerization of the vinylaluminum products to yield the more stable *trans*-adduct also seems to be catalyzed by nickel salts; this holds especially for phenylethynyl substrates. Finally, the nickel-catalyzed hydralumination appears to be somewhat less selective than the uncatalyzed reaction, as to the kinetically controlled *cis–trans* ratio (Table 1) and as to orientation of hydride addition to 1-phenylpropyne(*supra*). When this slight sacrifice in selectivity is tolerable, the nickel-catalyzed *cis*-hydralumination of internal alkynes represents a more convenient route to organic derivatives (alkenes, alcohols, acids, etc.) of vinylic aluminum systems[1-6].

In reflecting upon an explanation for this catalysis, we have arrived at a rational mechanism which also appears relevant to Ziegler's nickel-catalyzed dimerization of ethylene[7] (eqn.1):

$$(CH_3CH_2)_3Al + 3\ CH_2{=}CH_2 \xrightarrow[\text{pressure}]{100^\circ} (CH_3CH_2CH_2CH_2)_3Al \qquad (1a)$$

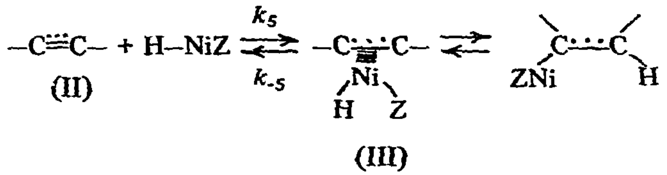
$$(CH_3CH_2CH_2CH_2)_3Al + 3\ CH_2{=}CH_2 \xrightarrow[\text{trace } H{-}C{\equiv}C{-}R]{NiZ_2} (CH_3CH_2)_3Al + 3\ CH_3CH_2CH{=}CH_2 \qquad (1b)$$

Ziegler has suggested that possibly this reaction may involve a two-body collision between $(C_4H_9)_3Al$ and the displacing olefin without the intervention of R_2AlH; Lucas has pictured a fanciful "sandwich" complex of dimeric R_3Al and nickel[8]. Since our findings show an accelerated addition of metal–hydrogen bonds to alkynes (k_5, *cf.* eqn.5), in comparison with Al–H bond addition, the reverse reaction (dissociation of vinyl–metal systems, k_{-5}) must also be accelerated (principle of microscopic reversibility). Therefore, our picture of the hydroalumination of alkynes, eqn. 3, 5 and 7 (R, R = iso-C_4H_9; II = alkyne; Z = acac), can be extended to explain the Ziegler dimerization in terms of an intermediate nickel hydride I via eqn. 2, 4, 5 and 6(R = C_2H_5; R' = H; II = excess C_2H_4 and Z = acac or C≡C–R). We assume that, analogous to k_5 for alkynes, k_4 and k_{-4} will be large for the alkylnickel/olefin + nickel hydride system. The salutary effect of R–C≡C–H on the nickel catalyst lifetime, observed by Wilke[7], may reside in the stabilizing influence of the nickel–acetylide σ-bond[9] on the key intermediate I (Z = C≡C–R).

$$(RR'CH{-}CH_2)_3Al + NiZ_2 \rightleftharpoons RR'CH{-}CH_2NiZ + (RR'CH{-}CH_2)_2AlZ \qquad (2)$$

$$R_2AlH + NiZ_2 \longrightarrow \underset{(I)}{H{-}NiZ} + R_2AlZ \qquad (3)$$

$$RCH_2CH_2NiZ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} H{-}NiZ + RCH{=}CH_2 \qquad (4)$$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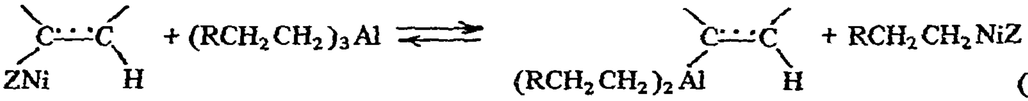
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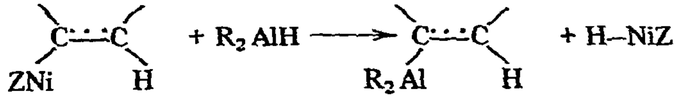
(7)

The fact that the catalyzed hydralumination yields ratios of *cis–trans* and orientational isomers of alkynes somewhat different than those of the uncatalyzed reactions can be interpreted to mean that a nickel hydride, rather than R_2AlH, is the attacking species. Recent reports on the skeletal rearrangements of homoconjugate dienes[10] and the olefin displacement reaction occurring with Grignard reagents[11] also suggest that these nickel-salt-catalyzed processes involve nickel hydride intermediates.

Further investigations on the transition-metal-catalyzed hydralumination of unsaturated hydrocarbons are being undertaken to establish the factors influencing the stereochemistry and the rate of addition, as well as the possible importance of putative π-complex intermediates (III). An alternative pathway to NiHZ, namely the formation of nickel(0) and its insertion into the Al–H bond (NiHZ, where Z = R_2Al), is also under active consideration. The formation of III, where Z = R_2Al, would be analogous to the mechanism proposed for the hydrosilation of olefins catalyzed by Group VIII metal complexes[12].

ACKNOWLEDGEMENT

We wish to express our appreciation to the Public Health Service for support of this research under Grant GM-14321.

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