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METAL CATALYSIS IN ORGANIC REACTIONS.VI.
NICKEL-CATALYZED REACTION OF TRIALKYLALANES WITH ALKYNYL BROMIDES: A CONVENIENT SYNTHESIS OF INTERNAL ALKYNES.

Giampaolo Giacomelli* and Luciano Lardicci

Centro di Studio del C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive-Istituto di Chimica Organica dell'Università,56100,Pisa,Italy.

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We were recently faced with the problem of investigating the role of some transition metal complexes in the reactions of acetylenic substrates with trialkylalanes:[1-3] in this context we reported that,under suitable experimental conditions,terminal acetylenes can be easily converted into dienes[1,3] or trialkylbenzenes[2] not readily available through conventional methods.We now wish to report that 1-bromo-1-alkynes,derived from terminal alkynes,react rapidly with trialkylalanes in the presence of 1.6 mol% of bis(N-methylsalycilaldimine)nickel $[Ni(mesal)_2]$ to afford the corresponding alkylated acetylenic substrate:

$$R_3Al \; + \; R'C{\equiv}CBr \xrightarrow[25^\circ C,\text{pentane}]{Ni(mesal)_2} R'C{\equiv}CR$$

This reaction seems to be applicable to a variety of alkylacetylenes and trialkylalanes,so providing a new synthetic route to internal alkynes.[4,5]

In the absence of nickel complexes,the reaction between triisobutylaluminum and 1-bromo-1-hexyne,at 25°C in pentane,is very slow:after 40 hrs the GLC analysis of the hydrolyzed reaction mixture shows,together with the unreacted alkynyl bromide(30%),the presence of 1-hexyne(42%) and of 2-methyl-4-nonyne[4](9%) and its carbalumination products(1,1-diisobutyl- and 1,2-diisobutyl-1-hexene)[6]. When the triisobutylaluminum was treated at 25°C in pentane with the same alkynyl bromide in the presence of $Ni(mesal)_2$,2-methyl-4-nonyne was formed within 1 hr in 83% yield together with 10% of 1-hexyne.Under these conditions the reaction of 1-bromo-1-alkynes with trialkylalanes proceeds always to give the desired internal alkyne.[6] The conversion of the reactions are quantitative and the yields are good in all cases,decreasing slightly only when 1-bromo-1-phenylacetylene is used. The experimental results are summarized in the Table.

TABLE

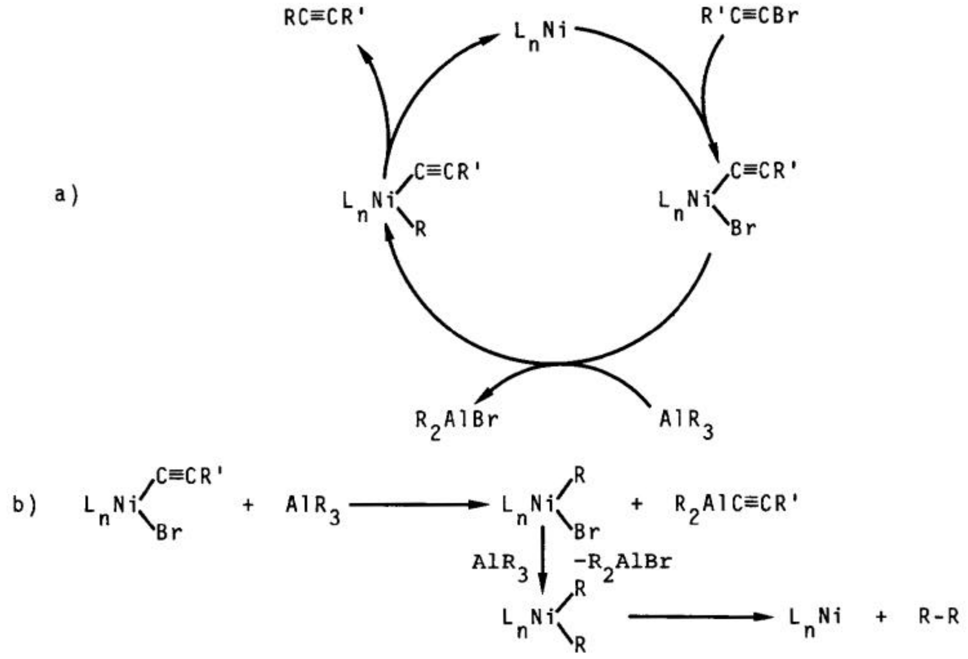
Entry[a]	R	R'	Product, yields%[b]	
			RC≡CH[c]	R'C≡CR
1	Bu^i	Bu^n	10	83(70)
2[d]			11	52
3		Bu^s	5	88(78)
4		$Bu^tCH(Me)$	4	90
5		Ph	12	42
6	Et	Bu^n	11	63
7		Bu^s	14	84(81)
8		Ph	27	55
9	$EtCH(Me)CH_2$	Bu^n	14	77(65)

[a] Unless otherwise stated, the reaction time is 1 hr. The amount of the catalyst is 1.6 mol% in all cases. [b] By GLC based on R'C≡CBr. The numbers in parentheses are isolated yields. In all cases, the alkane R-R was recovered in equivalent amounts with respect to the 1-alkyne. [c] Present as alkynylalane before hydrolysis. [d] 40 hrs at room temperature.

It is to observe that the yields of the reaction are critically dependent on the reaction time, the internal alkyne formed being able to react with the trialkylalane, in the presence of the Ni catalyst,[1,2] to afford higher molecular weight compounds, owing to competitive carbalumination and oligomerization processes. For istance, the yields of 2-methyl-4-nonyne dropped to 50% when the reaction was prolonged for 40 hrs (entry 2). Moreover all reactions afforded, along with the 1-alkyne (Table), an equivalent amount of a product, identified as the alkane derived from dimerization of the R alkyl group of the trialkylalane.

A tentative speculation on the reaction mechanism can be made based on both experimental results obtained and literature data.[7,8] First, it is reasonable to assume that the reaction of the trialkylalane with the Ni complex gives rise to the formation of Ni(0) species, probably through alkylated Ni complexes.[7] Second, the reaction may be regarded as a metal-catalyzed cross-coupling process:[8] so the reaction presumably proceeds through a catalytic cycle (Scheme) which consists of the oxidative addition of the alkynyl bromide to the Ni(0) species, followed by transmetalation and successive reductive elimination of the internal alkyne. On this basis, it seems likely that the alkynylalane and the alkane can be originated from competitive processes as shown in the Scheme.

SCHEME



However, irrespective of the precise mechanism, this synthetic procedure is really satisfactory, at least for the cases investigated. In fact, this metal-catalyzed reaction, even though it suffers as other methods[4] from the problem of utilizing only one of the three alkyl group of the organometallic reagent, offers an effective advantage in simplicity, as shown from the following representative preparation of 2,6-dimethyl-4-octyne.

To 0.0693g (0.21 mmol) of Ni(mesal)$_2$ in 10 ml of pentane were added sequentially, under N$_2$, 2.52g (12.7 mmol) of neat triisobutylaluminum (0°C, 1 min) and 2.05g (12.7 mmol) of 1-bromo-3-methyl-1-pentyne[9] dissolved in 15 ml of pentane (0°C, 10 min). After stirring for 1 hr at room temperature, the reaction mixture was cautiously hydrolyzed with diluted sulfuric acid and extracted with pentane.[10] The combined organic layers were washed twice with water, dried (Na_2SO_4) and carefully distilled to yield 1.37g (78%) of 2,6-dimethyl-4-octyne: bp 154°C, n_D^{25} 1.4261, mass spectrum m/e 138(M^+,26), 123(21), 109(58), 96(23), 95(26), 81(100), 67(67), 53(16). Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found C, 86.71; H, 13.08. The structure of the alkyne was further confirmed by conversion to (Z)-2,6-dimethyl-4-octene[9] through hydroalumination with diisobutylaluminum hydride.

References and notes

1. A.M.Caporusso,G.Giacomelli,and L.Lardicci,*J.Org.Chem.*,42,914(1977).
2. G.Giacomelli,A.M.Caporusso,and L.Lardicci,*J.C.S.Perkin Trans.1*,1333(1977).
3. A.M.Caporusso,L.Lardicci,and G.Giacomelli,*Tetrahedron Letters*,4351(1977).
4. A.Suzuki,N.Miyaura,S.Abiko,M.Itoh,H.C.Brown,J.A.Sinclair,and M.Midland, *J.Am.Chem.Soc.*,95,3080(1973).
5. E.Negishi and S.Baba,*J.Am.Chem.Soc.*,97,7385(1975).
6. All new products were adequately characterized by microanalytical and spectral data.3-Octyne was identified by comparison of its GLC retention time with that of an authentical sample.
7. Zh.I.Abramyan and G.A.Chukladzhyan,*Vysomol.Soed.*,14B,489(1972);A.Yamamoto, T.Yamamoto,T.Saruyama,and Y.Nakamura,*J.Am.Chem.Soc.*,95,4073(1973).
8. E.Negishi and S.Baba,*J.C.S.Chem.Commun.*,596(1976);S.Baba and E.Negishi, *J.Am.Chem.Soc.*,98,6729(1976);E.Negishi and D.E.Van Horn,*J.Am.Chem.Soc.*,99, 3168(1977);N.Okukado,D.E.Van Horn,W.L.Klima,and E.Negishi,*Tetrahedron Letters*, 1027(1978);A.O.King,E.Negishi,F.J.Villani,and A.Silveira Jr.,*J.Org.Chem.*,43,358(1978).
9. A.M.Caporusso,G.Giacomelli,and L.Lardicci,*Gazz.Chim.Ital.*,106,879(1976).
10. GLC analysis of the pentane extracts showed the presence of 2,5-dimethylhexane(5%),1-hexyne(5%),and of the internal alkyne(84%).