

METAL CATALYSIS IN ORGANIC REACTIONS. V.  
SELECTIVE ALKYLATION AND OLIGOMERIZATION OF ALIPHATIC 1-ALKYNES  
CATALYZED BY TRANSITION METAL SALTS.

Anna Maria Caporusso, Luciano Lardicci\* and Giampaolo Giacomelli.

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

(Received in UK 4 October 1977; accepted for publication 13 October 1977)

During recent studies on catalysis of organic reactions by metals<sup>1,2</sup> we have reported that the presence of small amounts of nickel complexes in the reaction between 1-alkynes (I) and triisobutylaluminium gives rise to the formation of a " head-to-tail " dimer, (E)-2,4-dialkyl-1,3-butadiene (V), and of trialkylbenzenes, whose relative yields are depending on the experimental conditions adopted.<sup>1</sup> The high selectivity of this nickel-catalyzed dimerization of 1-alkynes had suggested the use of this reaction as a synthetic route to optically active 2,4-dialkyl-1,3-butadienes of trans configuration, not otherwise available.<sup>2</sup>

In this context we have explored the influence of other soluble transition metal salts on the reactions between aliphatic 1-alkynes and triisobutylaluminium to check their eventual applications for preparative purposes.

The reactions were carried out in pentane at 25°C. The catalyst was prepared by adding the metal salt to a pentane solution of  $\text{AlBu}_3^i$  at -20°C; the alkyne was added to this mixture within 5 minutes. After 40 h<sup>3</sup> the reaction mixtures were hydrolysed with diluted sulphuric acid and the organic products, extracted with pentane, were analyzed by GLC. All the unknown compounds were identified through their IR, NMR and mass spectra.

The data obtained had shown that the course of the reaction is drastically changed in relation to the nature of the metal salt employed as catalyst (Table). In particular the presence of catalytic amounts of  $\text{FeCl}_3$  enhances the alkylative

T A B L E

R-C≡CH	MX <sub>n</sub>	Products, yields% <sup>a</sup>								
		III	IV	V	VI	VII	VIII	IX		
I	$\frac{\text{Al}}{\text{C}\equiv\text{C}}$ <sup>b</sup>									
R										
Pr <sup>n</sup> -CH <sub>2</sub> -	Ni(mesal) <sub>2</sub>	3	1	29	-	-	18	10		
EtCH(Me)-		-	2	66	-	-	14	3		
Pr <sup>n</sup> -CH <sub>2</sub> -	FeCl <sub>3</sub>	28	1	-	18	-	16	5		
		37	1	-	28	-	10	2		
EtCH(Me)-		33	2	2	31	-	8	1		
Pr <sup>n</sup> -CH <sub>2</sub> -	Mn(acac) <sub>3</sub>	-	-	-	-	73	10	9		
		-	-	-	-	78	6	6		
EtCH(Me)-		-	-	-	-	60	7	14		

<sup>a</sup> By GLC ( Se 301 ) of the reaction mixtures upon hydrolysis, other products being the reduction product (II) and

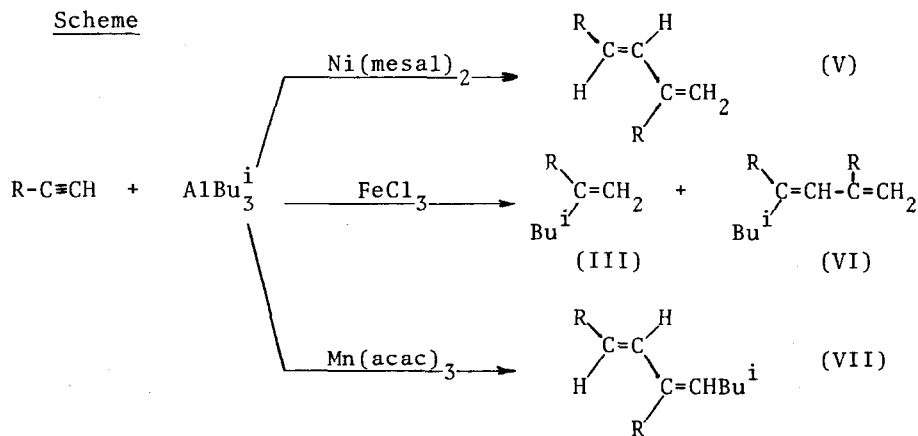
traces of linear oligomers. <sup>b</sup> (R-C≡CH)/(MX<sub>n</sub>) = 40 + 70.

properties of the organoaluminium compound. In fact, whereas the not-catalyzed reaction afforded in low yields the carbalumination products III and IV with a small prevalence of this last olefin,<sup>3</sup> in the presence of  $\text{FeCl}_3$  the 1-alkyne is completely converted with high regiospecificity into III and 2,4-dialkyl-4-isobutyl-1,3-butadiene (VI), together with small amounts of the reduction product (II) and of trialkylbenzenes VIII and IX (Table). Moreover linear trienes ( $\text{C}_{22}\text{H}_{40}$ , ca 12%) and tetraenes ( $\text{C}_{28}\text{H}_{50}$ , ca 7%), containing the isobutyl group from the aluminium alkyl, are recovered too. The yields of the products are dependent on the molar ratio  $\text{AlBu}_3^i$  to I: increasing this ratio decreases the formation of the cyclotrimers while increases the yields of both III and VI.

On the contrary I is essentially converted into 1,3-dialkyl-4-isobutyl-1,3-butadiene (VII) in the presence of  $\text{Mn}(\text{acac})_3$ : from the reaction mixtures, small amounts of the alkene II (5%) and of trialkylbenzenes are recovered too. Even in the manganese-promoted reaction the yields of VII seem to be depending on the molar ratio  $\text{AlBu}_3^i$  to I and on the structure of the acetylenic substrate. The conversion of 3-methyl-1-pentyne into VII occurs in fact with lower yields with respect to that of the 1-hexyne (Table).

Although the occurrence of alkylative processes seems to indicate that alkyl transition metal species are to be invoked in these metal catalyzed reactions, at present the rationalization of the data appears to be unwarranted.

The results obtained indicate a high selectivity of the reaction towards the formation of compounds having different structures and defined stereochemistry in relation to the different nature of the transition metal atom (Scheme).



The use of these reactions for the synthesis under mild conditions of substrates, such as VI and VII, not easily available through conventional method, is so claimed.

#### REFERENCES

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. L.Lardicci, A.M.Caporusso and G.Giacomelli, J.Organomet.Chem., 70, 333 (1974).