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METAL CATALYSIS IN ORGANIC REACTIONS. X.
NICKEL-CATALYZED DIMERIZATION OF 1-ALKYNES TO 1,3-DIALKYLBUTENYNES

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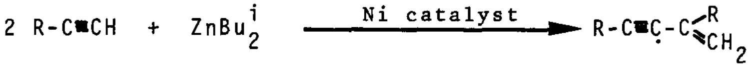
An efficient method for the selective synthesis of 1,3-dialkylbutenynes is described <u>via</u> reaction between terminal acetylenes and isolated diisobutylzinc in the presence of a nickel catalyst.

Considerable attention has been given to the dimerization processes of 1-alkynes: in addition to the well known Glaser[1] and Cadiot-Chodkiewicz[2] couplings to conjugated diynes, a number of interesting organometallic methods have been developed for the stereospecific dimerization of terminal alkynes to (E,E)-[3], (E,Z)-[4] or (Z,Z)-1,4-dialkyl-1,3-butadienes.[5] More recently useful methods for "head-to-tail" dimerization of 1-alkynes to 2,4-dialkylbutadienes in excellent yields were also reported.[6,7] However there appear presently to be only a few direct methods available for preparing conjugated enynes by dimerizing 1-alkynes. While both (Z)- and (E)-1,4-dialkylbutenynes can be obtained through the Straus procedure,[8] 1,3-dialkylbutenynes are described to be formed from 1-alkynes by using a chromium tetrabutoxide/diethylzinc catalyst.[9] During the course of our investigations, Carlton and Read reported a rhodium (I)-catalyzed dimerization of 1-octyne to 87% of the corresponding "head-to-tail" enyne along with 13% of the (E) isomeric enyne.[10]

We now wish to report some novel features of the catalysis of bis-[(N-methylsalycilaldimine)] nickel [Ni(mesal)$_2$] in the reaction of terminal acetylenes with organometallic compounds of main group elements. While nickel-catalyzed reaction of 1-alkynes with trialkylalanes provides a general route to (E)-2,4-dialkyl-1,3-butadienes, under suitable experimental conditions and by using isolated diisobutylzinc, 1-alkynes undergo a selective "head-to-tail" dimerization to afford 1,3-dialkylbutenynes in a generally good yield:

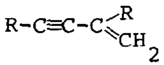


$$2\ \text{R-C}\equiv\text{CH} + \text{ZnBu}^{i}_{2} \xrightarrow{\text{Ni catalyst}} \text{R-C}\equiv\text{C-C}\begin{smallmatrix}\text{R}\\ \text{CH}_2\end{smallmatrix}$$

In the absence of nickel complexes, 1-hexyne reacts very slowly with diisobutylzinc and only little amounts of the alkynylzinc derivative are formed even at refluxing tetrahydrofuran (<25% after 24h). When diisobutylzinc was allowed to react with the stoichioimetric amount of 1-hexyne in the presence of 1,6 mol% of Ni(mesal)$_2$, the alkyne is slowly converted (36% after 72h) into 5-methylene-6-undecyne (66%), together with little amounts of (E)-5-methylene-6-undecene (4%) and 22% of a mixture of 1,3,5- and 1,2,4-tri-n-butylbenzenes. Whereas the conversion of the reaction is increased by raising temperature, yields are not significantly affected. The subsequent studies have indicated that the molar ratios $[\text{RC}\equiv\text{CH}]/[\text{ZnBu}^{i}_{2}] = 2$ and $[\text{RC}\equiv\text{CH}]/[\text{Ni(mesal)}_2] = 120$ give the most satisfactory results.[11] Thus, at 70°C, 1-hexyne is almost completely converted into the corresponding "head-to-tail" enyne with high yield (Table, entry 1). However, both conversion and yield of the reaction are depending on the structure of the acetylenic substrate employed (Table). In fact, increasing size of the alkyl group bound to the triple bond results in a progressive decreasing of the conversion, which is increased by raising temperature. Moreover, the yields in the dimer drop when β- or α- branched 1-alkynes are employed. This difficulty can however be overcome by carrying out the reaction in the presence of two equivalents of triphenylphosphine with respect to the nickel complex. The presence of this cocatalyst has a marked influence on both conversion and yield of the reaction (Table). For example, in the absence of PPh$_3$, 3-methyl-1-pentyne reacts very slowly to give a complex mixture of high oligomers, whereas under the same experimental conditions and in the presence of PPh$_3$, the 1-alkyne is converted (73%) into 3,7-dimethyl-4-methylene-5-nonyne in a good yield (Table, entry 11).

This synthetic procedure appears really satisfactory, taking also into account that the 1,3-dialkylbutenynes formed can be recovered in high chemical purity by simple distillation of the crude reaction mixture. Moreover, such a nickel-catalyzed dimerization offers the advantage of the use of a readily available catalyst, respect to other procedures.[9,10] The following representative procedure indicates the simplicity of the present method.

TABLE



$R-C{\equiv}C-C(R){=}CH_2$

Entry[a]	R	Temp. (°C)	in the absence of PPh_3		in the presence of PPh_3[c]	
			Conversion%[b]	Yield%[b]	Conversion%[b]	Yield%[b]
1	$n\text{-}C_4H_9\text{-}$	70	87	90		
2	$n\text{-}C_6H_{13}\text{-}$	70	61	96		
3		98.5	91	92	100	98 (95)
4	$n\text{-}C_8H_{17}\text{-}$	70	36	97 (96)		
5		98.5	81	95	100	97
6	$C_2H_5CH(CH_3)CH_2CH_2\text{-}$	70	86	94 (90)		
7	$C_2H_5CH(CH_3)CH_2\text{-}$	70	22	78 (66)		
8		70	41[d]	78		
9		98.5	79	68	95	85
10	$C_2H_5CH(CH_3)\text{-}$	70	<5	traces		
11		98.5	8	traces	73	54 (47)

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[a] Unless otherwise stated, the reaction time is 24h. The amount of the nickel complex is 0.83 mol% with respect to the 1-alkyne in all cases. All compounds were characterized by IR, NMR and mass spectra. [b] By GLC. The numbers in parentheses are isolated yields. [c] Two equivalents of PPh_3 were used with respect to the nickel complex.

[d] After 48h.

To 0.07g (0.21 mmol) of $Ni(mesal)_2$ in 20ml of anhydrous heptane were added, at 0°C under argon, 0.11g (0.42 mmol) of PPh_3, followed by 2.26g (12.6 mmol) of neat diisobutylzinc and 2.78g (25.2 mmol) of 1-octyne. The orange solution was heated at refluxing heptane for 24h and then cautiously hydrolyzed with dilute sulfuric acid and extracted with pentane. The combined organic layers were washed with saturated aqueous $NaHCO_3$,water,dried (Na_2SO_4) and carefully distilled to yield 2.64g (95%) of pure 7-methylene-8-pentadecyne.[10]

We are presently exploring the possible mechanism of the reaction, in particular for what concerns the role of the organozinc compound.

REFERENCES AND NOTES

1. C.Glaser,*Chem.Ber.*, 2, 422 (1869) ; *Annalen*, 137, 154 (1870).
2. W.Chodkiewicz and P.Cadiot, *Compt.Rend.*, 241, 1055 (1955).
3. G.Zweifel and R.L.Miller, *J.Am.Chem.Soc.*, 92, 6678 (1970);E.Negishi and T.Yoshida, *J.C.S. Chem.Comm.*, 606 (1973); Y.Yamamoto, H.Yatagai, and I.Moritani, *J.Am.Chem.Soc.*, 97,5606 (1975); R.C.Larock and J.C.Bernhardt, *J.Org.Chem.*, 42,1680 (1977).
4. G.Zweifel, N.L.Polston, and C.C.Whitney,*J.Am.Chem.Soc.*,90,6243 (1968); E.Negishi, G.Lew, and T.Yoshida, *J.C.S.Chem.Comm.*, 874 (1973).
5. G.Zweifel and N.L.Polston, *J.Am.Chem.Soc.*, 92,4068 (1970).
6. A.M.Caporusso, G.Giacomelli, and L.Lardicci, *J.Org.Chem.*, 42,914 (1977); G.Giacomelli, A.M.Caporusso, and L.Lardicci, *ibid*, 44,231 (1979).
7. R.C.Larock and B.Riefling, *J.Org.Chem.*, 43,1468 (1978).
8. F.Straus, *Annalen*, 137,154 (1870).
9. N.Hagihara, M.Tamura, H.Yamazaki, and M.Fujwara, *Bull.Chem.Soc.Japan*, 34,892 (1961).
10. L.Carlton and G.Read, *J.C.S. Perkin 1*, 1631 (1978).
11. At molar ratios $[RC{\equiv}CH]$ / $[ZnBu^{i}_{2}]$ higher than 2, the conversion of the reaction is complete after 24h at 70°C, but significant amounts of high oligomers are formed too.

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