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INCORPORATION OF CARBON DIOXIDE IN ALKYNE OLIGOMERIZATION CATALYZED BY NICKEL(0) COMPLEXES. FORMATION OF SUBSTITUTED 2-PYRONES

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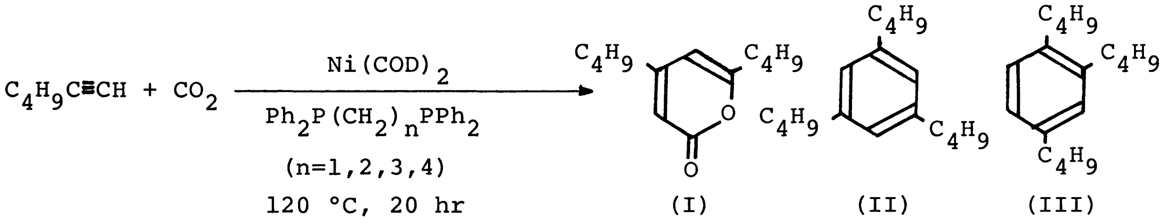
1-Hexyne and carbon dioxide were allowed to react with the catalyst system, Ni(COD)$_2$[COD=1,5-cyclooctadiene]-Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n=1,2,3,4), to give 4,6-dibutyl-2-pyrone together with 1-hexyne oligomers.

Catalytic fixation of CO$_2$ in organic compounds by transition metals to form a new C-C bond between them is a fascinating subject. However this has not been reported in the literature except one example in which butadiene was reacted with a palladium-phosphine complex in the presence of CO$_2$ to give a lactone.$^{1)}$ In this communication we wish to show another example of the fixation of CO$_2$ in alkynes by nickel(0) complexes.

When 1-hexyne was reacted with Ni(COD)$_2$-Ph$_2$P(CH$_2$)$_n$PPh$_2$(n=1,2,3,4) system in benzene at 120 °C under CO$_2$ initial pressure of 50 kg/cm^2 for 20 hr, 4,6-dibutyl-2-pyrone (I) was obtained together with 1-hexyne oligomers(See Table 1).



The structure of the pyrone was confirmed by the following spectral data and elemental analysis [IR; 1735(νC=O), 1642, 1560 cm^{-1}(νC=C): UV(EtOH); λmax 202(ε 6090), λmax 290 nm(ε 2350): ^{1}H-NMR; 4.33, 4.44 τ(olefinic)]. The other possible isomers of the pyrone were not detected.

The addition of 4 molar ratio of the ditertiary phosphine with n=4 to Ni(COD)$_2$ increased the yield of the pyrone compared with that of 2 molar ratio of the phosphine (See Run 5 and 6). In the case of triphenylphosphine or the ditertiary phosphine with n=6 or 10, the incorporation of CO$_2$ was very small. 1-Butyne reacted also with CO$_2$ in the presence of Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$ complex under a similar condition to give 4,6-diethyl-2-pyrone but phenyl- or diphenylacetylene did not give any CO$_2$ incorporated product.

Table 1 Reaction of CO_2 with 1-hexyne by $Ni(COD)_2$-$Ph_2P(CH_2)_nPPh_2$ system[a)]

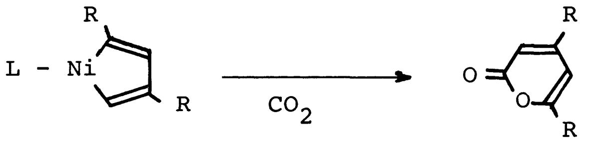
Run No	n for $Ph_2P(CH_2)_nPPh_2$	$Ph_2P(CH_2)_nPPh_2$/Ni (molar ratio)	1-hexyne recovered(%)	Products(%)[b)] (I)	(II)	(III)
1	1	2	8.1	1.7	9.6	1.1
2	2	2	5.2	3.7	18.2	3.8
3	2[c)]	2	36.1	1.0	3.9	1.1
4	3	2	4.9	4.8	15.0	2.2
5	4	2	9.3	6.6	18.8	2.5
6	4	4	1.0	9.3	16.4	3.3

a) 1-hexyne 3 ml, $Ni(COD)_2$ 0.4 mmol, solvent(benzene) 10 ml, CO_2(initial) 50 kg/cm^2; 120 °C, 20 hr.

b) The yields, based on 1-hexyne charged, were determined by glc. The other products (mainly higher oligomers of 1-hexyne) were not analyzed.

c) $Ni(Ph_2PCH_2CH_2PPh_2)_2$ complex 0.1 mmol was used.

We tentatively propose the following metalacyclopentadiene intermediate for this reaction in which the ditertiary phosphine coordiantes the central nickel atom.[2)]



L; $Ph_2P(CH_2)_nPPh_2$ (n=1,2,3,4) R; C_4H_9-, C_2H_5-

The attack of CO_2 on the intermediate leads to the pyrone formation[3)] whereas that of another acetylenic molecule on it results in the formation of oligomers. The coordination ability of the phosphine ligand may influence the selectivity of the products.

A cobalt complex, $HCo(Ph_2PCH_2CH_2PPh_2)_2$, is also effective for the pyrone formation though the yield of the pyrone is rather low compared to the corresponding nickel-ditertiary phosphine complex. An iron complex, $H_2Fe(Ph_2PCH_2CH_2PPh_2)_2$, is not effective for the pyrone formation.

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References

1) Y. Sasaki, Y. Inoue, and H. Hashimoto, J. C. S. Chem. Commun., 1976, 605.

2) J. J. Eisch and G. A.Damasevitz, J. Organometal. Chem., 96, C19 (1975);
J. J. Eisch and J. E. Galle, J. Organometal. Chem., 96, C23 (1975).

3) A similar reaction of CS_2(an isoelectronic compound of CO_2) with cobaltacyclopentadiene complexes to give 1,2-dithiopyrones has been reported;
Y. Wakatsuki and H. Yamazaki, J. C. S. Chem. Commun., 1973, 280.

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