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Preliminary communication

A NEW CATALYTIC SYNTHESIS OF NON-CONJUGATED ALKENYNES

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Summary

A new synthesis of alk-1-en-4-ynes catalyzed by nickel(0) complexes under mild conditions is described. The catalyst appears to be particularly sensitive to ligands, and to their ability to undergo dissociation from the metal.

Alk-1-en-4-ynes (I) are versatile reagents in organic chemistry. Stoichiometric syntheses from allyl halides and alk-1-ynes involving metalated species have been described [1]. A catalytic synthesis, which generally leads to low yields with low turn-over numbers, involves the use of copper(I) salts in the presence of stoichiometric amounts of neutralizing agents for hydrogen halides [2].

We now report a new catalytic synthesis of alk-1-en-4-ynes under mild conditions, starting with allylic esters of organic acids RCOOH and alk-1-ynes and requiring nickel(0) complexes as catalysts:

$$R'CH{=}CHCH_2OCOR + R''C{\equiv}CH \rightarrow R'CH{=}CHCH_2C{\equiv}CR'' + RCOOH$$

(I)

Yields are generally satisfactory, turn-over numbers reach values near 50 in some cases, and neutralizing agents are not needed. Various types of inert solvents such as ethers, esters or nitriles can be used. Allylic halides are unsatisfactory in this synthesis, but give products in low yield in the presence of neutralizing agents. Stoichiometric reactions of aryl halides and alk-1-ynes with nickel(0) complexes have been reported [3], however.

Ligand efficiency varies greatly with the ligand structure. Triisopropyl phosphite appears to be the best ligand among phosphites and phosphines. Further improvements have been achieved using allylic esters of but-3-enoic acid as substrates instead of allylic acetates or their homologues (Table 1).

The catalytic system may give rise to two parasitic reactions, namely coupling of the allylic groups and oligomerization (cyclo-trimerization) or polymerization of the alkynes. These reactions predominate in the case of acetylene and propargylic esters.

TABLE 1

SYNTHESIS OF ALK-1-EN-4-YNES FROM ALK-1-YNES AND ALLYLIC BUT-3-ENOATES IN TETRAHYDROFURAN IN THE PRESENCE OF TETRAKIS(TRIISOPROPYL PHOSPHITE)NICKEL(0)

RC≡CH (mmol)	Allylic ester[a] (mmol)	Catalyst (mmol)	Solvent (ml)	T (°C)	t (h)	RC≡CAll Yield(%)[b]	Turn-over number
R = Ph(2.0)	AA(2.0)	0.06	10	75	6	84	28
R = Ph(3.0)	AB(3.0)	0.06	10	75	6	90	45
R = Ph(2.5)	AB(2.5)	0.05	10	20	48	93	46.5
R = Ph(6.6)	CB(6.6)	1.00	20	75	4	60[c]	4
R = Ph(10.0)	BB(10.0)	1.00	20	75	4	64[d]	7
R = n-C_6H_{13}(1.5)	AB(1.5)	0.06	10	75	10	68	17
R = n-C_6H_{13}(2.5)	AB(2.5)	0.06	10	20	96	77	32
R = n-C_6H_{13}(1.8)	DB(1.8)	0.60	10	75	4	40[e]	1.2
R = $Me_2C(OH)$(3.5)	AB(3.5)	0.10	10	20	48	60[f]	21
R = $(CH_2)_5C(OH)$(3.0)	AB(3.0)	0.12	10	75	10	75[g]	18
R = $MeCOO(CH_2)_6$(1.2)	BB(1.2)	0.12	10	75	4	68[h]	7

[a] Abbreviations: All = allylic group; AA = allyl acetate; AB = allyl but-3-enoate; CB = crotyl but-3-enoate; BB = but-1-en-3-yl (CH_2=CHCH(Me)) but-3-enoate; DB = dec-2-enyl but-3-enoate. [b] Conversion of alkynes is almost complete unless otherwise indicated. [c] 6-Phenylhex-2-en-5-yne 29% and 5-phenyl-3-methylpent-1-en-4-yne 31%. [d] 6-Phenylhex-2-en-5-yne 34% and 5-phenyl-3-methylpent-1-en-4-yne 30%. [e] Octadec-8-en-11-yne 21% and 8-vinylhexadec-9-yne 19%; conversion 60%. [f] Estimated yield. [g] A small amount of this compound dehydrates; conversion 90%. [h] 14-Acetoxytetradec-2-en-5-yne 35% and 13-acetoxy-3-methyltridec-1-en-4-yne 33%; conversion 80%.

The effect of ligands on the catalytic behaviour of the complex is shown in Table 2. Very small differences in ligand structure cause large changes in yields and turn-over numbers. Thus the yield of phenylpentenyne at room temperature passes from traces to 92% on replacing triethyl phosphite by triisopropyl phosphite.

The most probable mechanism involves oxidative addition of the allylic ester to nickel (which would be favoured by the assistance of the 3-double bond of but-3-enoic acid), coordination and insertion of the alkyne, and hydrogen transfer from the original triple bond to the oxygen of the carboxylate anion, possibly via a nickel hydride intermediate. The positive effect of phosphite ligands is probably connected with the last reductive elimination step and not with the oxidative addition, for the latter would imply that phosphines should be the most effective ligands. The ability to dissociate off, thus favouring coordination of the substrate, can explain the different behaviour observed on passing from triethyl phosphite to triisopropyl phosphite. Tolman [4] reports equilibrium constants in benzene for the formation of the corresponding triphosphitenickel from tetraphosphitenickel complexes of $<10^{-10}$ and 2.7×10^{-5}, respectively.

Finally, alkyne reaction by insertion rather than by replacement of the carboxylate anion, followed by coupling of alkynyl and allyl groups, seems to be more likely in view of the fact that, under the same conditions and in the absence of alkynes, allyl but-3-enoate inserts the double bond into the allylnickel bond [5], according to the equation:

$$CH_2{=}CHCH_2\,COOCH_2\,CH{=}CH_2 \xrightarrow{\text{cat}} CH_2{=}CHCH_2\,CH_2\,CH{=}CHCOOH$$

The reactions were carried out for a few hours at room temperature or at reflux under nitrogen. Products were separated by conventional procedures and

TABLE 2

LIGAND EFFECT ON REACTION OF PHENYLACETYLENE WITH ALLYLIC ESTERS IN THF (20 ml, at 20°C for 48 h, except otherwise indicated)

PhC≡CH (mmol)	Allyl but-3-enoate (mmol)	Catalyst[a] (mmol)	PhC≡CCH$_2$CH=CH$_2$ yield(%)[b]	Turn-over number
5.0	5.0	$(TPP)_4Ni$ (0.1)	7[c]	3.5
5.0	5.0	$(TBP)_4Ni$ (0.1)	35[d]	18
5.0	5.0	$(TEPho)_4Ni$ (0.1)	traces	
1.0	1.0	$(TEPho)_4Ni$ (0.1)	1.5	
1.0	1.0	$(TEPho)_4Ni$ (0.1)	75[e]	7.5
5.0	5.0	$(TiPrPho)_4Ni$ (0.1)	92	46
5.0	5.0	$(TPhPho)_4Ni$ (0.1)	traces	
1.0	1.0	$(TPhPho)_4Ni$ (0.1)	24[e]	2.4
5.0	5.0	$Ni(COD)_2$ (0.1) + TiPrPho (0.2)	70	35
5.0	5.0	$Ni(COD)_2$ (0.1) + TiPrPho (0.3)	92	46
5.0	5.0	$Ni(COD)_2$ (0.1) + TiPrPho (0.4)	90	45

[a] Abbreviations: TPP = triphenylphosphine, TBP = tributylphosphine, TEPho = triethyl phosphite, TiPrPho = triisopropyl phosphite, TPhPho = triphenyl phosphite, COD = cycloocta-1,5-diene. [b] Conversions are near to quantitative unless otherwise indicated. [c] 42% Conversion; formation of trimers of phenylacetylene. [d] 54% Conversion; formation of trimers of phenylacetylene. [e] At 75°C for 6 h.

identified by IR, NMR and mass spectrometry and by comparison with known products [1,2]. Hydrogenation and ozonolysis gave the expected compounds. The following compounds were not described previously: Undec-1-en-4-yne. IR (film) (cm^{-1}): 1650, 990, 920; NMR (CCl_4, TMS), δ (ppm): 5.4—6.1 (m, 1H, CH=), 4.8—5.4 (m, 2H, $=CH_2$), 2.7—3.0 (m, 2H, $CH_2C=C$), 1.9—2.3 (m, 2H, $CH_2C\equiv C$), 1.1—1.7 (broad signal, 8H, CH_2), 0.7—1.1 (m, 3H, CH_3); Mass spectrum: M^+ 150, *m/e* 121, 109, 107, 93, 79, 77, 67, 55. 5-(1-Hydroxy-1-cyclohexyl) pent-1-en-4-yne. IR (film) (cm^{-1}): 2240, 1650, 990, 915; NMR (CCl_4, TMS), δ (ppm): 5.4—6.1 (m, 1H, HC=C), 4.8—5.4 (m, 2H, $=CH_2$), 3.4 (s, OH), 2.8—3.0 (m, 2H, $CH_2C=C$), 1.1—2.0 (m, 10H, CH_2); Mass spectrum: M^+ 164, *m/e* 149, 135, 121. 14-Acetoxy-tetradec-2-en-5-yne. NMR (CCl_4, TMS), δ (ppm): 5.2—5.7 (m, 2H, HC=CH), 3.9 (t, 2H, OCH_2, J 6 Hz), 2.6—2.9 (m, 2H, $CH_2C=C$), 2.0—2.2 (m, 2H, $CH_2C\equiv C$), 2.0 (s, 3H, CH_3COO), 1.7 (dd, 3H, CH_3, J_{vic} 5 Hz, J_{all} 1 Hz), 1.1—1.5 (broad signal, 12H); Mass spectrum: M^+ absent, *m/e* 189, 175, 161, 147, 133, 119, 107, 105, 94, 79. 13-Acetoxy-3-methyltridec-1-en-4-yne. NMR (CCl_4, TMS), δ (ppm): 5.4—6.0 (m, 1H, HC=), 4.8—5.4 (m, 2H, $=CH_2$), 3.9 (t, 2H, OCH_2, J 6 Hz), 2.9—3.2 (broad m, 1H, $CHCH_3$), 2.0—2.2 (m, 2H, $CH_2C\equiv C$), 2.0 (s, 3H, CH_3COO), 1.3—1.6 (m, 12H, CH_2), 1.2 (d, 3H, CH_3, J 7Hz); Mass spectrum: M^+ absent, *m/e* 189, 175, 161, 147, 133, 119, 107, 105, 94, 79. 6-Phenylhex-2-en-5-yne and 5-phenyl-3-methylpent-1-en-4-yne. IR (film) (cm^{-1}): 2220, 990, 970, 920; NMR (CCl_4, TMS), δ (ppm): 7.0—7.5 (m, 5H, aromatic), 5.4—6.1 (m, 2H, HC=CH and 1H, HC=C), 4.8—5.4 (m, 2H, $=CH_2$), 3.1—3.5 (m, 1H, $HC(CH_3)C=CH_2$), 2.9—3.1 (m, 2H, $CH_2C=C$), 1.6 (dd, 3H, $C=CCH_3$, J_{vic} 5 Hz, J_{all} 1 Hz), 1.3 (d, 3H, CH_3, J 7Hz); Mass spectrum: M^+ 156, *m/e* 141, 128, 115, 101, 91. Octadec-8-en-11-yne and 8-vinylhexadec-9-yne. NMR (CCl_4, TMS), δ (ppm): 5.4—6.0 (m, 2H, HC=CH and 1H, HC=C), 4.8—5.4 (m, 2H, $C=CH_2$), 2.9—3.2 (m, 1H, HCC_7H_{15}), 2.6—2.9 (m, 4H, $CH_2C=CCH_2$), 1.8—2.3 (m, 2H, $CH_2C\equiv C$), 1.1—1.7 (m, 18H, CH_2 and 20H, CH_2), 0.8—1.1 (m, 6H, CH_3); Mass spectrum: M^+ 248, *m/e* 219, 205, 191, 177, 163, 149, 135, 121, 107, 93, 79, 67, 55.

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