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Synthesis of Diynes by Phase Transfer Catalysis in the Presence of a Pd (0) Catalyst.

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Abstract A new method for diynes preparation by phase transfer catalysis in the presence of a Pd (0) catalyst is described

INTRODUCTION

Diacetylenes deserve considerable interest, both from the point of view of their chemistry[1], and of the solid state properties of their homopolymers[2]

The synthesis of diynes can be achieved by oxidative dimerization of acetylenes[3-6], by reaction of organolithium compounds with 1-alkynyl ethers[7], of complexes of aluminium acetylides with CuBr[8] or of lithium dialkyl diaryl borates with iodine[9]

We wish to report a new method for diynes preparation by PTC in the presence of a Pd (0) catalyst, namely, bis (dibenzylideneacetone) palladium (0), according to Scheme 1

$$\underset{\mathbf{1}}{CH_3(CH_2)_n{-}C{\equiv}C{-}H} \;+\; \underset{\mathbf{2}}{Br{-}CH_2{-}CH{=}CH_2} \;\xrightarrow[N_2\text{ , }CH_2Cl_2\text{ / 50\% aq. NaOH}]{n\text{-}Bu_4NBr\text{ , }Pd(dba)_2}$$

$$\longrightarrow \underset{\mathbf{3}}{CH_3(CH_2)_n{-}(C{\equiv}C)_2{-}(CH_2)_nCH_3} \;+$$

a/ n = 2, b/ n = 3, c/ n = 4, d/ n = 5, e/ n = 6, f/ n = 7.

$$+\; \underset{\mathbf{4}}{CH_3(CH_2)_n{-}C{\equiv}C{-}CH_2{-}CH{=}CH{-}(CH_2)_3{-}C{\equiv}C{-}(CH_2)_nCH_3}$$

a/ n = 2, b/ n = 3, c/ n = 4.

Scheme 1

RESULTS AND DISCUSSION

The reaction shown in Scheme 1 did not occur in the absence of allyl bromide and diynes **3a-3f** were not detected when the phase transfer catalyst was not present

The yields of diynes depend on the amount of allyl bromide used. If allyl bromide was present in catalytic amounts diynes were obtained in excellent yields (74-90 % determined by GC) , when its amount was raised, working at 1 1 molar ratio alkyne allyl bromide the yield of diynes **3** decreased (10-15 %) while the endiynes **4** were detected by GC in high yield (70-75 %)

The results of our experiments are shown in Table 1

One of the most useful applications of palladium in organic chemistry is a consequence of the fact that π-allyl palladium complexes are easily formed starting with various organic substrates that contain at least one double bond. In the case of the reaction of Pd (0) catalyst with allylic substrates, only a replacement of the allylic leaving group by another group is possible[10-12]

Table 1. Diynes and endiynes prepared by PTC in the presence of Pd(dba)$_2$

Entry	n from $CH_3(CH_2)_n$	alkyne-allyl bromide molar ratio	Yield[a] % (compound)
1	2	12 5	80 (3a)
2	3	idem	85 (3b)
3	4	idem	90 (3c)
4	5	idem	90 (3d)
5	6	idem	78 (3e)
6	7	idem	75 (3f)
7	2	1 1	70 (4a)[b]
8	3	idem	75 (4b)[b]
9	4	idem	72 (4c)[b]

[a] Determined by GC

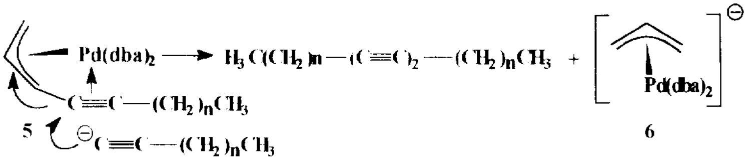
[b] The reaction product contains 10 - 15 % of the corresponding diyne.

It is well known that PTC alkylation can be performed in presence of concentrated aqueous sodium hydroxide, weak acids like the acetylene compounds (pK$_a$ 22-25) leading to anions[13,14].

Taking into account the above mentioned facts we presume that the formation of diynes can be explained by the following mechanism (Scheme 2)

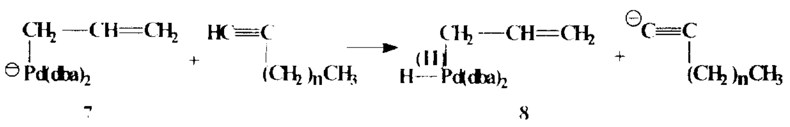
-first, the allyl bromide is attacked by the deprotonated alkyne, to give an intermediate with enyne structure, which immediately forms the π complex **5** with palladium.

-second, the complex **5** undergoes a nucleophilic substitution, in which the π-allyl palladium complex moiety acts as a leaving group, and the alkyne anion is the nucleophile.



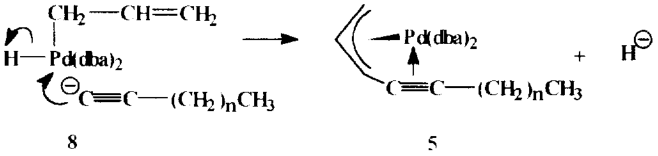
Scheme 2

The existence of the anionic palladium species **6** was proved by Pietropaolo and coworkers[15]. The species **6** will regenerate the neutral species, probably by producing Pd (II) species **7**, which will extract one proton, more likely from the alkyne, leading to species **8** (Scheme 3)



Scheme 3

The Pd (II) species **8** further undergoes the nucleophilic attack of the alkyne anion and thus the complexed enyne **5** will be regenerated (Scheme 4)



Scheme 4

Similar changes of Pd (0) species to Pd(II) species were presumed to account for the mechanism of palladium-catalyzed addition of activated nucleophiles to allenes[16]. The propensity of palldium (0) catalyst to abstract and to donate hydride ion is also well known[17a-c].

The formation of endiyne at 1:1 molar ratio between alkyne and allyl bromide, can be rationalized by the reductive dimerization of complexed enyne, initially formed, which is now present in a higher concentration. The mechanism of this reaction is now under study and the results will be published elsewhere.

The structure of endiyne with a triple bond nonconjugated with a double bond was established by comparison of ^{1}H-NMR spectra of conjugated and nonconjugated enynes. The nonconjugated alkyl enynes which have a single methylene group between the triple and the double bond show a multiplet between 2.85-3.20 ppm[14,18]. By percolating the raw reaction product dissolved in hexane through a silicagel column, then concentrating the obtained hexane solution and carefully drying under vacuum to remove any residual hexane and traces of lower boiling reactants, we managed to obtain a mixture which contains only the diyne (10-15%) and endiyne (85-90 %). The ^{1}H-NMR spectrum of such a mixture presents a doublet in the 2.90-3.00 ppm region (see experimental.)

In conclusion, we have observed that Pd(dba)$_2$ is an excellent catalyst for preparation of diynes under very mild conditions and in high yields, a π-allyl complex acting as a catalyst for the reactions which occur in organic phase.

EXPERIMENTAL

Spectral data and analyses. ^{1}H-NMR resonance spectra were recorded on a GEMINI 300 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal standard. IR spectra were recorded on a UNICAM SR 200 G instrument using CCl_4 as solvent. GC and MS analyses were performed on a HEWLETT PACKARD 5890 (GCL)-5972(MSD) using a HP-5MS 30 m x 0.25 mm x 0.25 μm capillary.

Reagents. The reactions were carried out under nitrogen. All reagents were obtained commercially, except Pd(dba)$_2$ which was prepared according to literature data.

General Procedure for PTC Preparation of Diynes 3a-3f. To a degassed mixture of 50% aqueous NaOH (10 mL), CH_2Cl_2 (40 mL), n-Bu_4NBr (2 mmol), 1-alkyne (0.02 mol) and allyl bromide (1.6mmol), Pd(dba)$_2$ (5 mol%) was added and the resulted mixture was magnetically stirred under nitrogen at room temperature for 24h. The organic phase was separated and dichloromethane was removed by rotary evaporation. The oily residue was dissolved in hexane, washed with brine, dried over $MgSO_4$ and chromatographed on silica gel column (250-400 mesh) with hexane. The hexane solution was concentrated by rotary evaporation and carefully dried under vacuum to remove any residual hexane and traces of lower boiling reactants. The purity and composition of the oily reaction products was determined by gas chromatography and mass spectral analyses. The purity of chromatographed material was good enough for NMR spectra.

4,6-Decadiyne (3a): ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, 6H, J=7 Hz), 1.35 (m, 4H), 2.15 (m, 4H); MS, m/z : 105, 119, 134 (M^+)

5,7-Dodecadiyne (3b): ^{1}H-NMR ($CDCl_3$) δ 0.95 (t, 6H, J=7 Hz), 1.40 (m, 8H), 2.10 (m,4H) ; MS, m/z 133, 147, 162 (M^+)

6,8-Tetradecadiyne (3c): ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, 6H, J=7 Hz), 1.35 (m, 8H), 1.50 (m, 4H), 2.20 (m, 4H) ; MS, m/z 119, 133, 147, 190 (M^+)

7,9-Hexadecadiyne (3d): ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, 6H, J= 7H), 1.20-1.70 (m, 16H), 2.20 (m, 4H); MS, m/z : 133, 147, 161, 175, 218 (M^+)

8,10-Octadecadiyne (3e) : ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, 6H, J=7 Hz), 1.2-1.75 (m, 20H), 2.20 (m, 4H) ; MS, m/z : 147, 161, 175, 189, 202, 246 (M^+)

9,11-Icosadiyne (3f): ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, 6H, J=7 Hz), 1.15-1.80 (m, 24H), 2.20 (m, 4H); MS, m/z : 161, 175, 189, 203, 217, 231, 274 (M^+)

General Procedure for Preparation of Endiynes 4a-4c. The procedure for preparation and purification of endiynes was similar to that used for diynes, except that this time the molar ratio alkyne: allyl bromide was 1:1. The reaction was performed at 0.02 mole scale. After purification the resulting oily mixture contains only endiyne (85-90%) and diyne (10-15%) and was analyzed by ^{1}H-NMR

7-Hexadecene-4,12-diyne (4a): ^{1}H-NMR ($CDCl_3$) δ 2.95 (m, 4H), 5.50 (m, 1H), 5.85 (m, 1H) ; IR ν_{max} (CCl_4) 950, 1660, 2120 and 3100 cm^{-1} , MS, m/z 77, 79, 91, 103, 105, 115, 117, 131, 145, 159, 173, 187, 201, 216 (M^+)

8-Octadecene-5,13-diyne (4b): ^{1}H-NMR ($CDCl_3$) δ 2.90 (m, 4H), 5.55 (m, 1H), 5.85 (m, 1H) ; IR ν_{max} ($CHCl_3$) : 955, 1665, 2125 and 3120 cm^{-1} , MS, m/z 77, 79, 91, 103, 105, 115, 131, 145, 159, 173, 187, 201, 215, 229, 244 (M^+)

9-Icosaene-6,14-diyne (4c): ^{1}H-NMR ($CDCl_3$) δ 2.95 (m, 4H), 5.50 (m, 1H), 5.80 (m, 1H) ; IR ν_{max} ($CHCl_3$) : 950, 1663, 2123 and 3110 cm^{-1} , MS, m/z 77, 79, 91, 103, 105, 117, 131, 145, 159, 201, 215, 272 (M^+)

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