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SELECTIVE CATALYSTS FOR THE TRIMERIZATION OF CONJUGATED ACETYLENES

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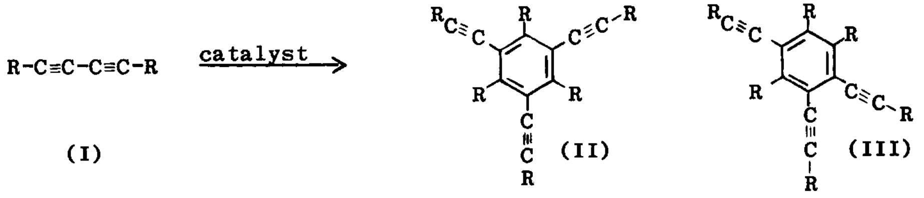
There is considerable interest in the chemistry of multifunctional acetylenes,[1] but synthetic routes to these materials can be quite complicated.[2,3] The catalytic trimerization of conjugated acetylenes (I) offers a simple preparation of a range of compounds (eq. 1),[4,5] but yields are poor and separation of the two isomers (II) and (III) is difficult.



(1)

We have now found that the catalyst $[Ni(CO)_2(PPh_3)_2]$ produces solely the unsymmetrical isomer (III) in high yield (R=Me, 77%, R=Ph 83%). Mixtures of (II) and (III) may alternatively be obtained in high yield by using $CoCp(CO)_2$ as the catalyst.

For R=Me, the symmetrical isomer (II) has previously been prepared in 5% yield using a Ziegler catalyst for reaction 1,[5] while the use of $Hg[Co(CO)_4]_2$ gave yields of 8% (II) and 4% (III).[4]

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For R=Ph, yields of 21% (II) and 13% (III) have been obtained with Hg[Co(CO)$_4$]$_2$.[4] These appear to represent optimum yields however and in our hands the last reaction gave only a 10.0% yield of (II) and a small amount of (III) after a tedious separation by column chromatography. With a Ziegler catalyst, diphenylbutadiyne gave chiefly low molecular weight polymer (M.W. ~ 2,000) and some (III).

These low yields result from the reactivity of (II) and (III) to the above catalysts, since we have found that similar low molecular weight polymers result from the reaction of (I), (II) or (III) (R=Ph) in the presence of a Ziegler catalyst. The formation of these polymers is not surprising since the more active catalysts will trimerize disubstituted acetylenes.

A high selectivity for (II) and (III) is possible only for the less reactive catalysts which are capable of trimerizing (I) but are insensitive to (II) or (III). Besides Ni(CO)$_2$(PPh$_2$)$_2$, we have found that CoCp(CO)$_2$ fulfills these conditions. In this case, (I) (R=Ph) gave a mixture from which was obtained a 16% yield of (II) and a 72% yield of (III).

The following example is typical of the use of Ni(CO)$_2$(PPh$_3$)$_2$. To 1.0 g diphenylbutadiyne in 30 ml benzene was added 0.10 g catalyst and the solution refluxed under nitrogen for 10 hours. Elution with benzene from an alumina column, evaporation and recrystallization from acetone gave 0.83 g (83%) of 1.2.4-*tris*-phenylethynyl-3.5.6-triphenylbenzene m.p. 226° (lit. 227-228°).[4]

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