A Singular Substituent Effect in the Nickel(0) mediated Cocyclisation of Octa-1,7-diynes with Alkynols. One-step Synthesis of Tetralin Lactones from Acyclic Precursors

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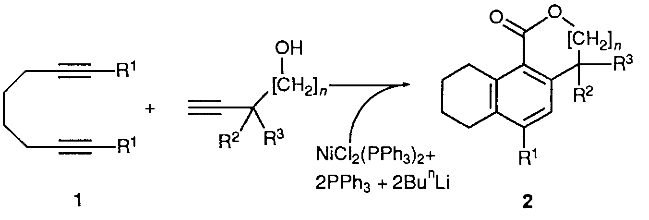
Whereas the reaction of simple octa-1,7-diynes is fruitless, those bearing ester groups on the terminal positions react with alkynols in the presence of stoichiometric amounts of a nickel(0) reagent derived from $NiCl_2(PPh_3)_2$ and Bu^nLi to give tetralin lactones in moderate to good yields.

Hepta-1,6-diynes may be cocyclised with monoalkynes to give indane derivatives in the presence of Co^{I} (stoichiometric),[1] Rh^{I} (catalytic),[2] or Ni^{0} (stoichiometric)[3] complexes in good yields. The analogous reaction with octa-1,7-diynes is largely unsuccessful when $ClRh^{I}(PPh_3)_3$[2] is used but proceeds well with Co^{I} complexes.[1,†] Here we report that the success of the reaction with these latter diynes mediated by Ni^{0} is dependent critically on the presence of a terminal ester group on the diyne and that, with alkynols as the monoalkyne components, moderate to good yields of tetralin lactones can be produced in one step.

Reaction of octa-1,7-diynes **1**, R^1 = H, Me, Et, COMe, COPh, CH(OH)Ph, CH_2CH_2OH or SMe, with prop-2-ynyl alcohol failed to give any cocyclised product. In stark contrast, dimethyl and diethyl deca-2,8-diyn-1,10-dioate **1**, R^1 = CO_2Me, and CO_2Et gave the lactones **2a**‡ and **2b**‡ as white solids, m.p.s 120–122 °C and 62 °C respectively. The combina-



Scheme 1

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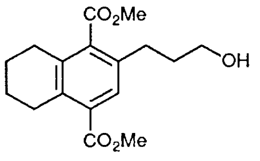
† The monoalkyne must bear two trimethylsilyl groups for good yields of the tetralin to be obtained.

‡ All new compounds gave satisfactory microanalyses or high resolution mass spectra.



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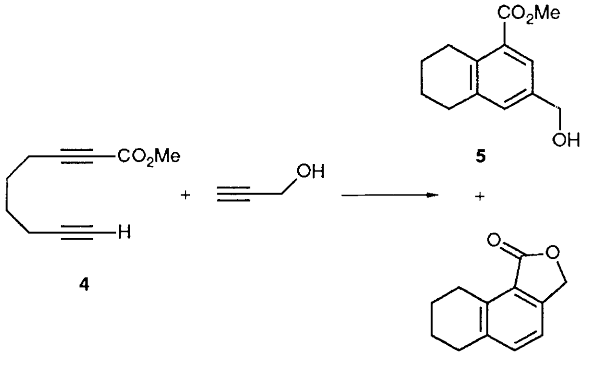

Scheme 2

tion of cyclisation and lactonisation (Scheme 1) appears to be general for propynylic alcohols as the monoynes (Table 1, entries 3–5) and also proceeded, albeit in reduced yield, with a homopropargylic one (entry 6). The specific substituent effect of the ester group is clearly not the result of pre-esterification of the alkynol with the diester since pent-4-yn-1-ol gives a respectable yield (42%) of the cyclisation product **3**‡ without lactonisation. This point is emphasized by the result of the reaction of methyl nona-2,8-diynoate **4** with prop-2-ynyl alcohol in which the *meta*-substituted ester alcohol **5**‡ (72%) is formed in preference to the lactone **6** (19%) (Scheme 2). This reaction also shows that the minimum requirement for successful cocyclisation is one ester terminally substituted on the diyne.

Table 1 Synthesis of tetralin lactones **2** from octa-1,7-diyne esters **1**

Entry	Lactone **2**‡	*n*	R^1	R^2	R^3	Yield (%)
1	**a**	0	CO_2Me	H	H	78
2	**b**	0	CO_2Et	H	H	46
3	**c**	0	CO_2Me	Me	H	51
4	**d**	0	CO_2Me	Me	Me	58
5	**e**	0	CO_2Me	$-[CH_2]_5-$		58
6	**f**	1	CO_2Me	H	H	24

The exact reason for the enhancement of the cocyclisation effected by the ester groups is unclear. If the lack of reactivity of other octa-1,8-diynes is a consequence of bad orbital overlap as has been advanced for Rh^I cocyclisations,[2] then we must consider a change in mechanism for the reaction with the diyne-esters since the latter groups should not alter the conformation of the diyne.

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