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Nickel mediated Double Bond formation from *vic*-Dibromides and Ethyl Magnesium Bromide

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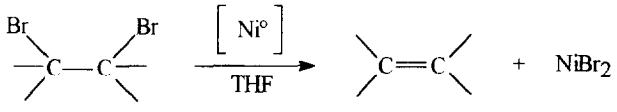
Abstract: *vic*-dibromides are quantitatively converted into alkenes by using a catalytic amount of $NidppeCl_2$, in the presence of two molar equivalents of EtMgBr in THF. Stereochemical aspects of the reaction are given.

The *vic*-dibromide-alkene functional group interconversion represents a useful step in the double bond protection-deprotection strategy[1]. The reagents usually employed in this reaction require stoichiometric amount of a suitable low valent metal or the use of a metal catalyst that must be regenerated in situ by a reducing agent[2].

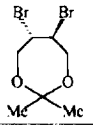
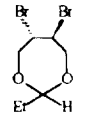
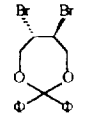
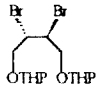
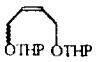
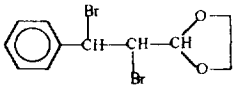
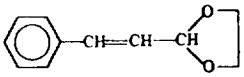
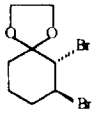
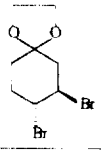
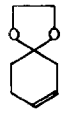
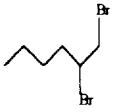
During our studies on the nickel mediated organic reactions[3], we found a new simple method to gain carbon-carbon insaturation starting from *vic*-dibromides, employing a catalytic amount of nickel 1,4-bis(diphenylphosphino)ethane dichloride ($NidppeCl_2$) and EtMgBr as source of Ni°.

Scheme 1



In a typical run, a solution of EtMgBr (0.021 mol) in anhydrous THF was slowly added to a solution of 0.01 mol of the suitable dibromide and $2 \cdot 10^{-5}$ mol of $NidppeCl_2$ in the same solvent (100 ml) at 0 °C. The reaction takes place instantaneously and, after the usual workup, gives the desired product with good yields (see Table).

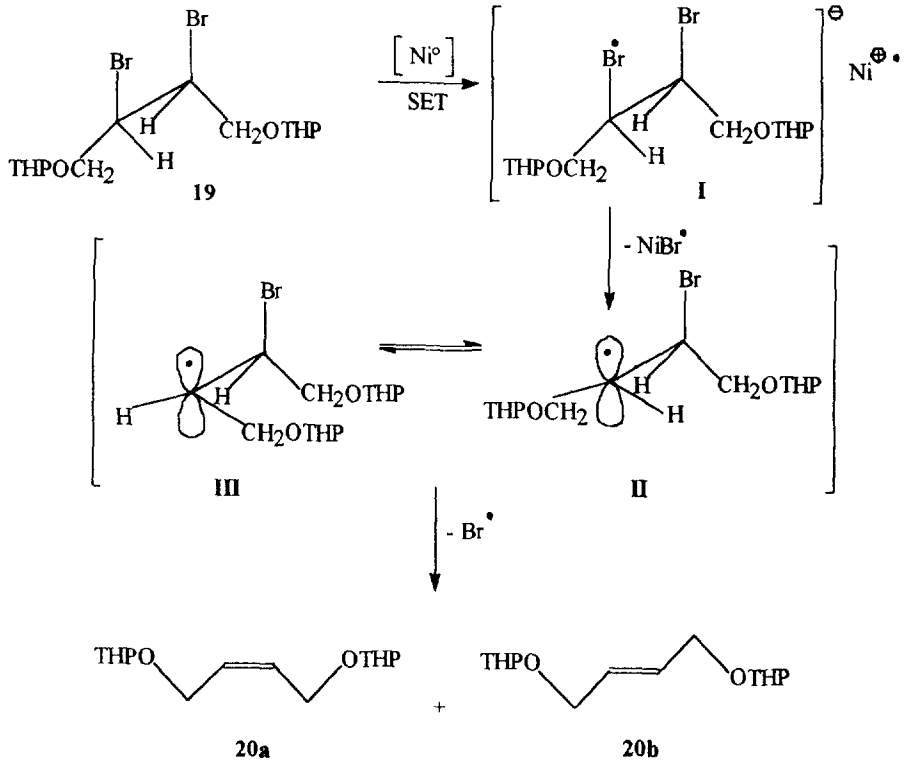
Table

Run	Substrate[a]		Product[b]		Rndt %[c]
1		1		2	100
2		3		4	80[d][e]
3		5		6	100
4		7		8	100
5		9		10	96
6		11		12	82
7		13		14	100
8		15		16[f]	100
9		17		18	100

Notes: (a) Obtained by bromination of the opportune alkene in CCl_4 at 0 °C with usual procedures[4]; (b) the structure of all the products are in accordance with ^1H-, ^{13}C-NMR at 200 and 50 Mhz respectively, gas-mass and FT-IR analyses; (c) on the purified products; (d) the by-product is the 2-ethyl-1,3-dioxep-4-ene (20%); (e) 3 moles of EtMgBr were required; (f) also obtained by thermal rearrangement of 14 at 150 °C for a few minutes.

The stereochemistry of the reaction was established reacting the *treo*-2,3-dibromo-1,4-tetrahydropyranyloxybutane (**19**)[5] in the conditions adopted above (Scheme 2).

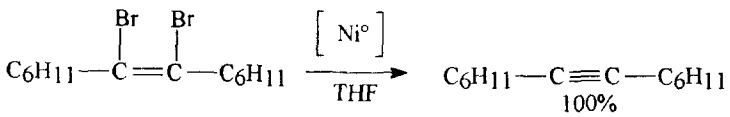
Scheme 2



The 1:1 cis/trans mixture of 1,4-ditetrahydropyranyloxybut-2-ene (**20**) obtained seems to be in accordance with a SET process in which the radical anion **I** gives the two radicals **II** and **III**, direct precursors of **20**.

It must be underlined that the reaction seems to be also effective to convert alkenyl dibromides into alkynes without by-products (Scheme 3)

Scheme 3



The advantages obtainable with this procedure are: **(a)** the short reaction times (ranging between few seconds and fifteen minutes); **(b)** the absence of isomerization of double bonds generally taking place when Pd-catalysts[6] are used; **(c)** the absence of reactivity with esters and carbonyl compounds[7]; **(d)** the high yields obtained with respect to what reported for the use of the Grignard reagents[8], **(e)** the possibility to carry out the reaction in the presence of the tetrahydropyranyloxy group on the contrary to what reported for similar reaction conditions[9], **(f)** the extremely mild reaction conditions adopted to generate triple bonds.

Acknowledgements

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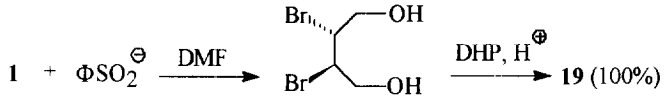
5) Compound **19** with the correct stereochemistry was obtained reacting **1** with one mole equivalent of sodium sulfinate in DMF at 60 °C for 3 h.The reaction cannot affect the C-Br bonds for stereochemical reasons. After hydrolysis the alcohol **21** was protected with DHP giving only the *treo* **19**.



21 (90%)

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