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CARBON-CARBON BOND FORMATION BETWEEN 1,3-DIENES AND ELECTRON DEFICIENT ALKENES

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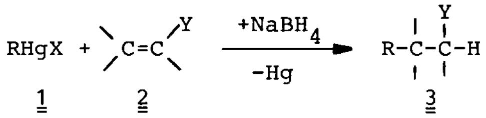
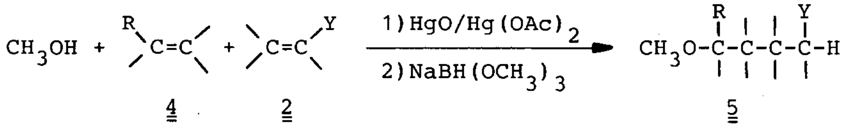
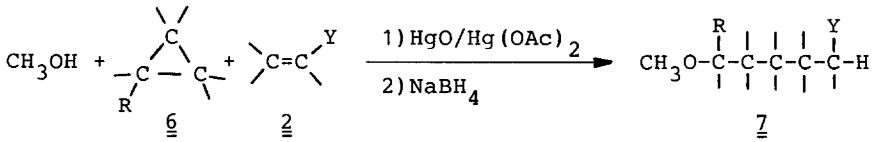
Abstract: 1,3-Dienes and electron deficient alkenes are coupled in a one pot carbon-carbon bond formation reaction under mild conditions.

Reductions of alkylmercuric salts 1 with $NaBH_4$ in the presence of electron deficient alkenes 2 yield products 3[1] in a carbon-carbon bond formation reaction via alkyl radicals R•[2].

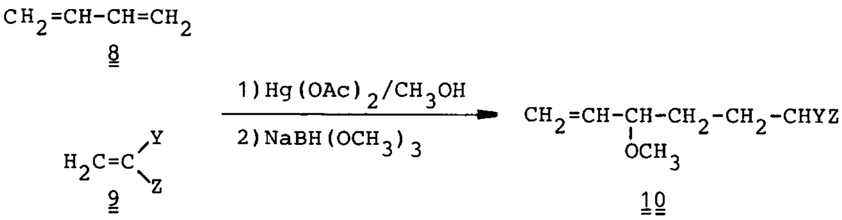


Using this method solvomercuration[3] of alkenes 4 and cyclopropanes 6 followed by a reduction in the presence of alkenes 2 leads to products 5[4] and 7[5]





We have now shown that also butadiene 8 can be coupled with alkenes 9 to give products 10 in one pot syntheses.



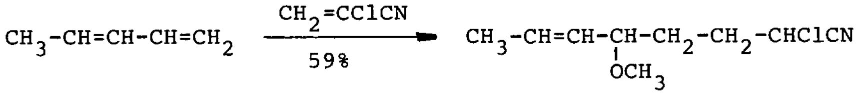
A 1:1 HgO/$Hg(OAc)_2$ mixture is combined with a threefold excess of butadiene 8 in methanol between -10 and 20°C. After decolouration of HgO methanol is destilled off, alkene 9, dissolved in CH_2Cl_2 (10% solution), is added in three fold excess and the reduction is carried out with two equivalents of $NaBH(OCH_3)_3$ at 0°C (0.5-1.0 h). Filtration and destillation yield products 10 (Table I).

Table I

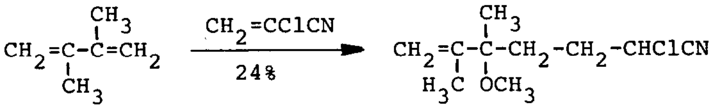
Overall yields and spectra of products 10 in the reaction of butadiene 8 with alkenes 9.

Alkenes 9 Y	 Z	Products 10 (Yield, %)	^{1}H-NMR(δ) OCH_3	IR(cm^{-1}) C≡N	 C=O
H	CN	47	3.26	2260	
H	CO_2CH_3	34	3.26		1745
H	$COCH_3$	22	3.25		1710
CH_3	CN	24	3.26	2240	
Cl	CN	60	3.28	2250	

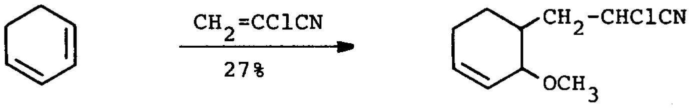
Substituted dienes can be used also.



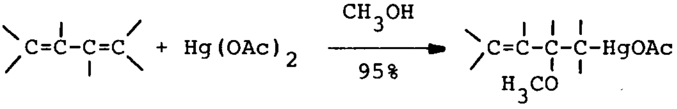
$$CH_3\text{-}CH{=}CH\text{-}CH{=}CH_2 \xrightarrow[59\%]{CH_2{=}CClCN} CH_3\text{-}CH{=}CH\text{-}\underset{\displaystyle OCH_3}{CH}\text{-}CH_2\text{-}CH_2\text{-}CHClCN$$



$$CH_2{=}\underset{\displaystyle CH_3}{C}\text{-}\overset{\displaystyle CH_3}{C}{=}CH_2 \xrightarrow[24\%]{CH_2{=}CClCN} CH_2{=}\underset{\displaystyle H_3C}{C}\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OCH_3}{C}}\text{-}CH_2\text{-}CH_2\text{-}CHClCN$$



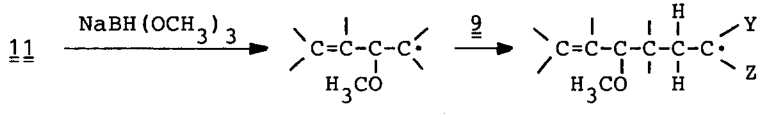
Products are formed in good yields ($CH_2=CClCN$: 60%) with butadiene 8 and 1-alkylbutadiene. Two alkyl groups in position 1,4 or 2,3 reduce the yield in coupling experiments with 1-chloroacrylonitrile to 25%. The reason for these poor yields is not the solvomercuration step that proceeds in all cases with about 95%.



$$>C=C-C=C< + Hg(OAc)_2 \xrightarrow[95\%]{CH_3OH} >C=C-\underset{H_3CO}{C}-C-HgOAc$$

11

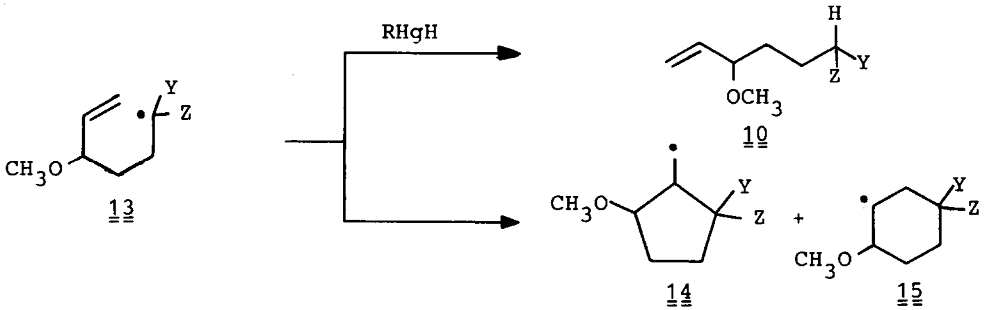
Reduction of 11 yields homoallyl radicals 12 that add to alkenes 9 and give 5-hexenyl radicals 13.



$$11 \xrightarrow{NaBH(OCH_3)_3} >C=C-\underset{H_3CO}{C}-C\cdot \xrightarrow{9} >C=C-\underset{H_3CO}{C}-C-\overset{H}{\underset{H}{C}}-C\cdot<^{Y}_{Z}$$

12 13

5-hexenyl radicals 13 can either abstract a hydrogen (13 → 10) or cyclize (13 → 14 + 15)[6].



13 10 14 15

The cyclic radicals 14 + 15 react with further alkene 9 and give products of higher molecular weight. It is this competition between H-abstraction and cyclization of the 5-hexenyl radical 13 that seems to influence the yield of 1:1-products.

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