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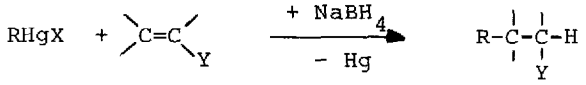
CARBON-CARBON BOND FORMATION BETWEEN ALKYLATED ALKENES AND ACRYLIC ESTER VIA 2-METHOXYALKYL RADICALS

Bernd Giese+ and Klaus Heuck

Institut für Organische Chemie und Biochemie
Technische Hochschule Darmstadt
Petersenstraße 22, D-6100 Darmstadt, Germany

Summary: Methoxymercuration/demercuration reactions of alkenes 10 in the presence of acrylic ester yield products 11 in a carbon-carbon bond formation reaction.

Reductions of alkylmercuric salts 1 with $NaBH_4$ in the presence of electron deficient alkenes 2 yield products 3 in a carbon-carbon bond formation reaction$^{1)}$. In this synthetic method alkyl radicals 4, adduct radicals 5 and hydrogen donors 6$^{2)}$ are formed as intermediates. The reason for the formation of 3 is based on the different selectivities of radicals 4 and 5$^{1,3)}$ in the competition reaction with the hydrogen donor 6 and the alkene 2.

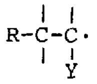


$$RHgX + >C{=}C\langle_{Y} \xrightarrow[-\ Hg]{+\ NaBH_4} R\!-\!\overset{|}{\underset{|}{C}}\!-\!\overset{|}{\underset{\underset{Y}{|}}{C}}\!-\!H$$

1 2 3

R·

4

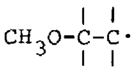


$$R\!-\!\overset{|}{\underset{|}{C}}\!-\!\overset{|}{\underset{\underset{Y}{|}}{C}}\cdot$$

5

RHgH

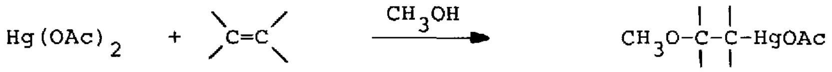
6



$$CH_3O\!-\!\overset{|}{\underset{|}{C}}\!-\!\overset{|}{\underset{|}{C}}\cdot$$

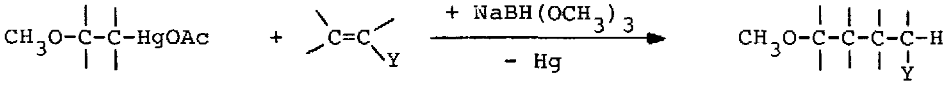
7

With methoxyalkylmercuric salts 8, generated in methoxymercuration reaction[4)] of alkenes (eq. a), products 9 are formed via 2-methoxyalkyl radicals 7 (eq. b)[5)].



$$Hg(OAc)_2 + {>}C{=}C{<} \xrightarrow{CH_3OH} CH_3O\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}HgOAc$$

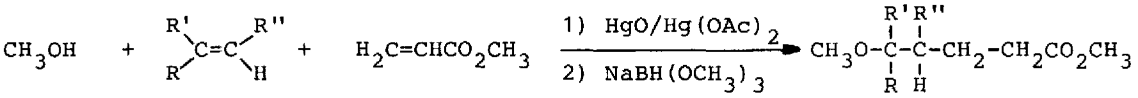
8 (a)



$$CH_3O\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}HgOAc + {>}C{=}C{<}^{}_{Y} \xrightarrow[-\ Hg]{+\ NaBH(OCH_3)_3} CH_3O\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{Y}{C}}\text{-}H$$

8 2 9 (b)

Experiments with alkylated alkenes 10 and acrylic ester have now shown, that this two step reaction (eq. a and b) can be carried out in a one flask synthesis (eq. c).



$$CH_3OH + \overset{R'}{\underset{R}{>}}C{=}C\overset{R''}{\underset{H}{<}} + H_2C{=}CHCO_2CH_3 \xrightarrow[2)\ NaBH(OCH_3)_3]{1)\ HgO/Hg(OAc)_2} CH_3O\text{-}\overset{R'}{\underset{R}{C}}\text{-}\overset{R''}{\underset{H}{C}}\text{-}CH_2\text{-}CH_2CO_2CH_3$$

10 11 (c)

A 1:1 HgO/Hg(OAc)$_2$ mixture is combined with an equivalent amount of alkene 10 in methanol. After decolouration of HgO methanol is distilled off and acrylic ester, dissolved in CH_2Cl_2 (10% solution), is added in tenfold excess. The reduction is carried out with an equivalent amount of NaBH(OCH$_3$)$_3$ at room temperature (1-3 h). Filtration and distillation yield the products 11 (Table I).

HgO is important, because it neutralizes the acetic acid that is set free during the methoxymercuration and that can reverse addition reaction (a)[6].

Table I

Overall yields and spectra of products 11 in the methoxymercuration/ demercuration reactions of alkenes 10 in the presence of acrylic ester.

Alkenes 10			Products 11	^{1}H-NMR (δ)		IR (cm^{-1})
R	R'	R"	(Yield,%)	CO_2CH_3	OCH_3	$\nu_{C=O}$
H	H	H	50	3.67	3.32	1745
H	C_4H_9	H	48	3.65	3.29	1745
H	C_6H_5	H	50	3.63	3.21	1735
H	$-(CH_2)_3-$		65	3.70	3.30	1750
H	$-(CH_2)_4-$		58	3.66	3.30	1740
CH_3	C_3H_7	H	30	3.68	3.14	1745
CH_3	H	CH_3	53	3.66	3.29	1745
CH_3	CH_3	CH_3	32	3.67	3.16	1750

The overall yields of the one flask synthesis (c) are with unsubstituted, mono- and 1,2-dialkylated alkenes 10 between 48 and 65%, with 1,1-disubstituted and trialkylated alkenes 10 about 30% (Table I). With tetraalkylated alkenes this synthetic method fails because product mixtures arise.

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