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CC BOND FORMATION REACTIONS WITH UMPOLUNG OF ALDEHYDES VIA RADICALS

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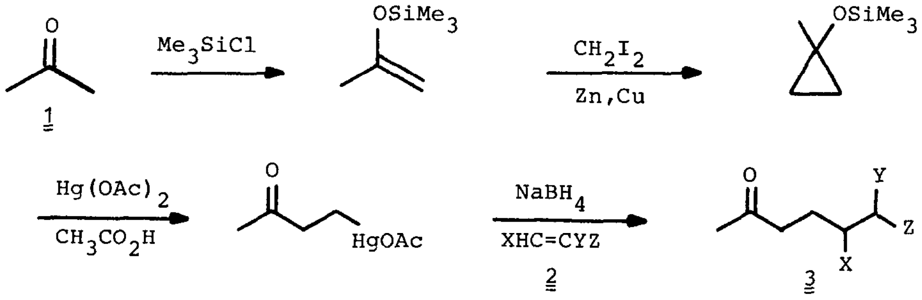
Summary: Aldehydes 4 and alkenes 2 yield 1,6-heterosubstituted products 7 and/or 9. The CC bond formation occurs by reactions of radicals 10 which rearrange very rapidly to radicals 12.

Ketones 1 can be transformed into ketones 3 via silylation[1)], cyclopropanation[2)], mercuration[3)] and radical CC bond formation with alkenes 2[4)].



We have now observed that in a similar reaction sequence aldehydes 4 yield products 7 via cyclopropanes 5 and coupling products 6 which are desilylated with KF in acetone (Table I).

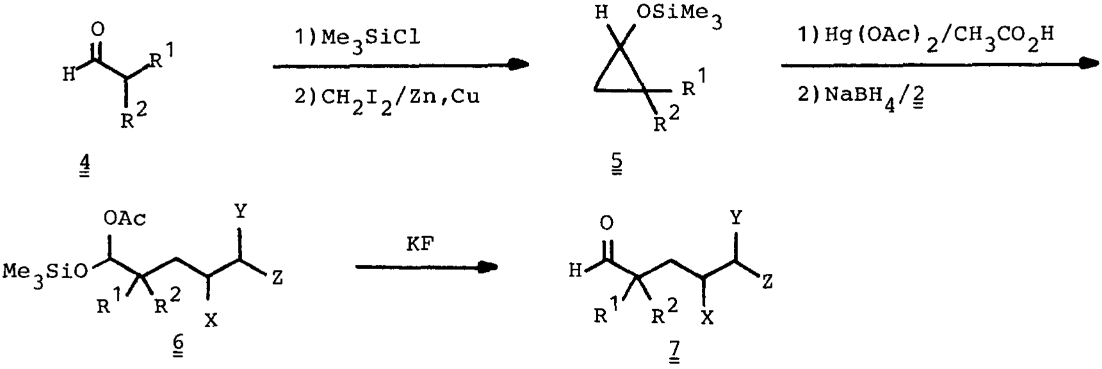


Table I

Products 7 from cyclopropanes 5 and alkenes 2 via solvomercuration in CH_3CO_2H.

Cyclopropanes 5		Alkenes 2			Products 7	^{1}H NMR (δ)	IR (cm^{-1})
R^1	R^2	X	Y	Z	(Yields,%)	CHO	$\nu_{C=O}$
C_4H_9	H	H	H	CN	60	9.61	1720
C_4H_9	H	H	H	CO_2CH_3	52	9.58	1720,1735
C_4H_9	H	H	H	$COCH_3$	61	9.53	1720
C_4H_9	H	H	Cl	CN	65	9.63	1720
C_4H_9	H	H	CH_3	CN	40	9.59,9.57	1715
C_4H_9	H	$CO_2C_2H_5$	H	$CO_2C_2H_5$	60	9.64,9.60	1715,1740
CH_3	CH_3	H	H	CN	51	9.48	1715
CH_3	CH_3	H	H	CO_2CH_3	49	9.48	1720,1735
CH_3	CH_3	H	Cl	CN	51	9.50	1720
CH_3	CH_3	H	CH_3	CN	30	9.50	1720
CH_3	CH_3	$CO_2C_2H_5$	H	$CO_2C_2H_5$	45	9.49	1720,1735

If the solvomercuration of cyclopropanes 5 is carried out in the presence of water, organomercuric salts 8 are formed that give aldehydes 7 and 9 after reductive coupling with alkenes 2 (Table II).

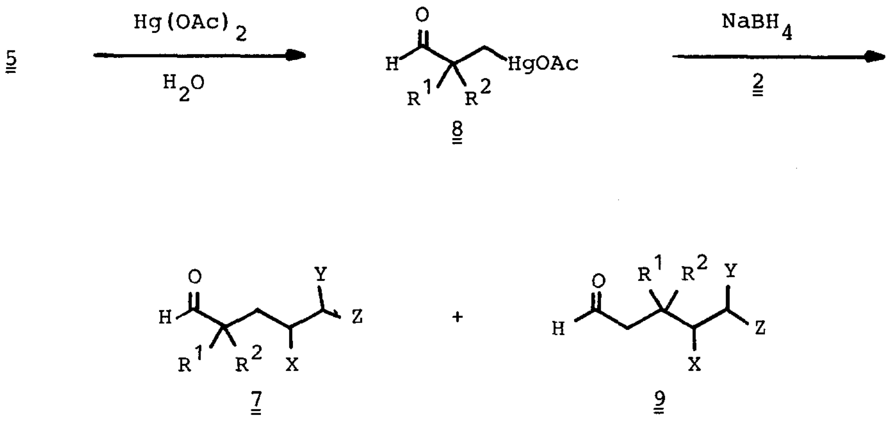
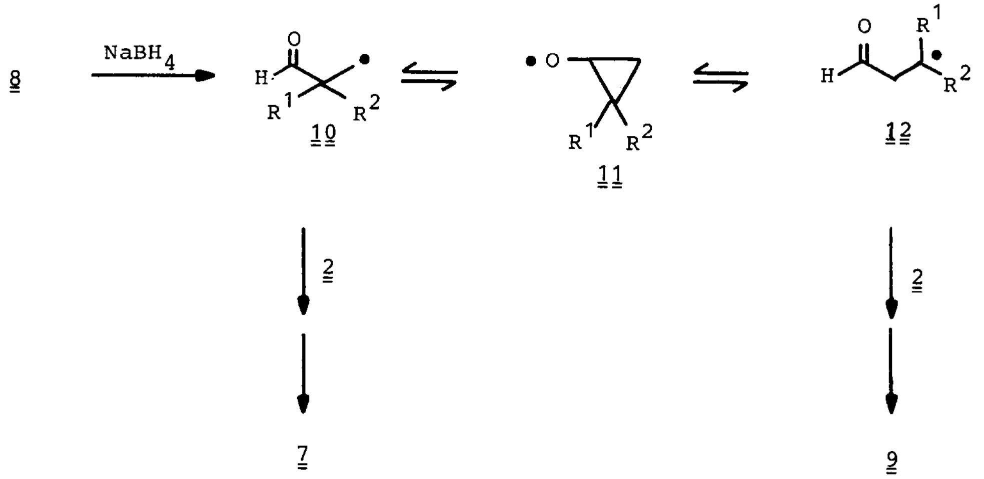


Table II

Products 7 and 9 from cyclopropanes 5 and alkenes 2 via solvomercuration in H_2O.

Cyclopropanes 5		Alkenes 2			Concentration of 2	Product ratio	Products 7 + 9
R^1	R^2	X	Y	Z	(mol/l)	7:9	(Yield,%)
C_4H_9	H	H	H	CN	3.0	78:22	55
C_4H_9	H	H	H	CN	0.33	24:76	55
C_4H_9	H	H	H	CO_2CH_3	3.0	78:22	50
C_4H_9	H	H	H	CO_2CH_3	0.33	18:82	45
C_4H_9	H	H	Cl	CN	3.0	89:11	35
C_4H_9	H	H	Cl	CN	0.33	51:49	32
C_4H_9	H	$CO_2C_2H_5$	H	$CO_2C_2H_5$	3.0	56:44	36
C_4H_9	H	$CO_2C_2H_5$	H	$CO_2C_2H_5$	0.33	19:81	33
CH_3	CH_3	H	H	CN	3.0	10:90	47
CH_3	CH_3	H	H	CN	0.33	4:96	40
CH_3	CH_3	H	H	CO_2CH_3	3.0	4:96	45
CH_3	CH_3	H	H	CO_2CH_3	0.33	<2:>98	40
CH_3	CH_3	H	Cl	CN	3.0	40:60	45
CH_3	CH_3	H	Cl	CN	0.33	4:96	40
CH_3	CH_3	$CO_2C_2H_5$	H	$CO_2C_2H_5$	3.0	7:93	42
CH_3	CH_3	$CO_2C_2H_5$	H	$CO_2C_2H_5$	0.33	<2:>98	45

The data in Table II show that the rel. yields of rearranged products 9 are higher with 0.33 than with 3.0 molar solutions of alkenes 2. This indicates that competing with the trapping of radicals 10 a rearrangement to 12 occurs in which cyclopropyloxy radicals 11 are the intermediates[5].



The rearrangement occurs quantitatively in the presence of 0.33 molar solution of acrylester and fumarester if $R^1=R^2=CH_3$. Therefore, in these systems either unrearranged or rearranged aldehydes 7 or 9 can be synthesized.

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