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$Co_2(CO)_8$ CATALYZED REACTION OF OXETANES WITH TRIALKYLSILANES

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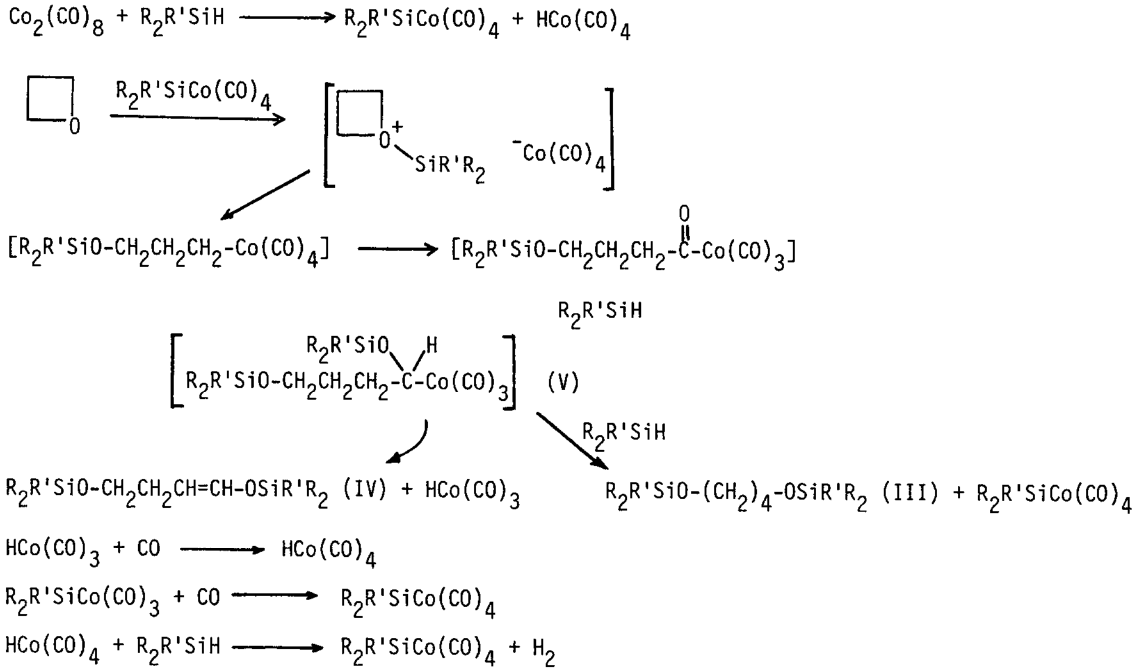
Summary: Dicobalt octacarbonyl catalyzed silyl-hydroformylation of oxetanes can be controlled by the choice of trialkylsilane. Triethylsilane gives 1,4-*bis*-silyl ethers while *t*-butyldimethylsilane yields silyl enol ethers.

The silyl-hydroformylation (Si-H/CO) reaction of THF with CO and Et_2MeSiH catalyzed by $Co_2(CO)_8$ has been reported to yield 1,5-*bis*-(diethylmethylsiloxy)pentane (I) or a mixture of Z- and E-1,5-*bis*-(diethylmethylsiloxy)pentene (II) depending on the choice of solvent.[2] Thus, the reaction in benzene gives I while in acetonitrile a mixture of Z- and E-II is obtained. On the other hand, the Si-H/CO reaction with oxetanes can not be controlled by choice of solvent.[2]

We find that the choice of R_3SiH permits control of the Si-H/CO reaction with oxetanes. For example, reaction of oxetane with Et_3SiH and CO catalyzed by $Co_2(CO)_8$ in benzene gives 1,4-*bis*-(triethylsiloxy)butane (III) (62%). This result is not unexpected since aliphatic epoxides have recently been reported to yield *bis*-silyl ethers of 1,3-diols under similar conditions.[3] We have also found that the Si-H/CO reaction of oxetane with *t*-Bu(Me)$_2$SiH gives a mixture of Z- and E-1,4-*bis*-(*t*-butyldimethylsiloxy)butene (IV)(2.5:1,59%).

We believe that these results can be rationalized in terms of the mechanism previously proposed with minor modifications. Thus reaction of R_3SiH with $Co_2(CO)_8$ is well known to yield $R_3SiCo(CO)_4$ and $HCo(CO)_4$.[4,5] Transfer of R_3Si from $R_3SiCo(CO)_4$ to the basic oxygen of the oxetane to yield an oxonium cation/$^-Co(CO)_4$ ion pair. Nucleophilic attack by $^-Co(CO)_4$ on an alpha carbon of the oxonium cation results in a 3-trialkylsiloxypropyl cobalt tetracarbonyl species which can undergo insertion of CO to yield a 4-trialkylsiloxybutyryl cobalt tricarbonyl species. Oxidative addition of a molecule of R_3SiH to the coordinately unsaturated cobalt center followed by hydrosilation of the acyl group would yield a 1,4-*bis*-(trialkylsiloxy)butyl cobalt tricarbonyl intermediate (V). Reaction of this with another molecule of R_3SiH would result in elimination of the III and regeneration of $R_3Si(CO)_3$. Alternatively, reductive elimination of $HCo(CO)_3$ from V would yield Z- and E-IV. Finally, reaction of $HCo(CO)_4$ with R_3SiH are known to yield $R_3SiCo(CO)_4$ and hyrogen.[5] Possibly, the difference in behavior of Et_3SiH and *t*-Bu(Me)$_2$SiH in these reaction results from steric hinderance to oxidative addition of *t*-Bu(Me)$_2$SiH to V. There should be no steric hinderance to reductive elimination of a silyl enol ether from V.

To a mixture of R_3SiH (3 eq) and $Co_2(CO)_8$ (0.05 to 0.2 eq) under CO (1 atm) was added a benzene solution of oxetane (1 eq). With Et_3SiH the reaction was run at rt for 4 h, while with *t*-Bu(Me)$_2$SiH the reaction was run at reflux. 1,4-*Bis*-(triethylsiloxy)butane,[6] Z-1,4-*bis*-(*t*-butyldimethylsiloxy)-1-butene,[7] and E-1,4-*bis*-(*t*-butyldimethylsiloxy)-1-butene.[8]



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7. NMR: δ 0.036 (s,6H), 0.0100 (s,6H), 0.875 (s, 9H), 0.902 (s, 9H), 2.33 (t of d, 2H, J=7.3 and 6.8 Hz), 3.58 (t, 2H, J=6.8 Hz), 4.08 (d of t, 1H, J=7.2 and 5.8 Hz), 6.20 (d of t, 1H, J=5.9 and 1.5 Hz). MS: m/e 259 (50%) M-tBu.
8. NMR: δ 0.025 (s, 6H), 0.106 (s, 6H), 0.869 (s, 9H), 0.891 (s, 9H), 2.068 (q, 2H, J=6.8 Hz), 3.54 (t, 2H, J=6.8 Hz), 4.936 (d of t, 1H, J=12 and 7.8 Hz), 6.25 (d of t, 1H, J=12 and 1 Hz). MS: m/e 259 (50%) M-tBu$^+$. Elemental Analysis of a mixture of Z and E isomers. Found: C, 60.49%; H, 11.66%. Calc. for $C_{16}H_{36}O_2Si_2$: C, 60.69% and H, 11.46%.

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