Tetrahedron Letters,Vol.23,No.9,pp 931-934,1982 0040-4039/82/090931-04$03.00/0
Printed in Great Britain

# SYNTHESIS OF 1,6-HETEROSUBSTITUTED PRODUCTS VIA RADICALS

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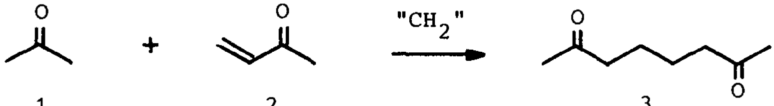
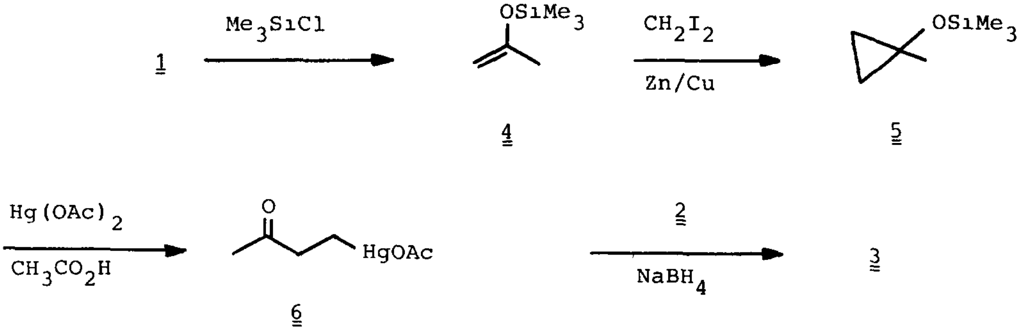
Summary: Ketones and electron deficient alkenes are combined with each other via a methylene group to yield 1,6-heterosubstituted products in a radical chain reaction.

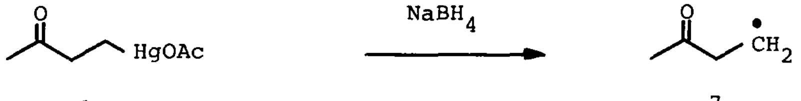
Syntheses of 1,6-heterosubstituted alkanes via carbon-carbon bond formation are reactions with "Umpolung"[1]. We have developed a new method, in which ketones 1 and electron deficient alkenes 2 are combined with each other by a methylene group to yield 1,6-substituted products.



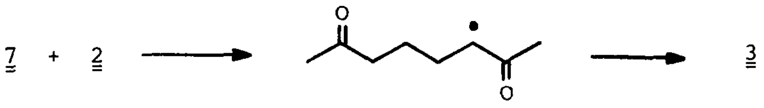
The synthetic route contains the steps a) silylation[2] of 1, b) cyclopropanation[3] of 4, c) mercuration[4] of 5 and d) reduction of 6 in the presence of 2.



The new carbon-carbon bond is formed in a radical chain reaction[5]. Radicals **7** are generated by reduction of organomercuric salts **6** with $NaBH_4$. Additions of **7** to alkenes **2** yield adduct radicals **8** which are trapped by H-donors to give products **3**. Organomercuric hydrides are believed to be the H-donors in reductions of organomercuric salts with $NaBH_4$[6].

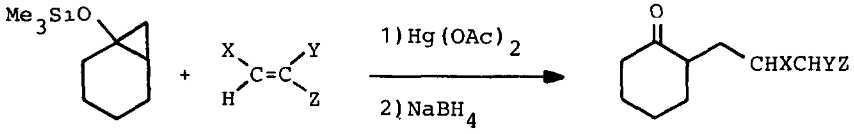


**6** **7**



**8**

The scope of this method has been tested by the reaction of cyclopropane **9** which is formed from cyclohexanone by standard procedures[2,3].



**9** **10** **11**

Equimolar amounts of **9** and $Hg(OAc)_2$ react at 20°C for 1 h in $CH_3CO_2H$. The acid is destilled off and alkene **10**, dissolved in $CH_2Cl_2$, is added in threefold excess. Reduction with a concentrated solution of $NaBH_4$ in water yields products **11** (Table I).

Table I

Yields and spectra of products 11 in the mercuration/demercuration reaction of cyclopropane 9 in the presence of alkenes 10.

| Alkenes 10 | | | Products 11 | $^1$H-NMR (δ) | IR (cm$^{-1}$) | |
|---|---|---|---|---|---|---|
| X | Y | Z | (Yield, %) | $CO_2CH_2R$ | $\nu_{C=O}$ | $\nu_{C\equiv N}$ |
| H | H | CN | 68 | | 1710 | 2245 |
| H | H | $COCH_3$ | 64 | | 1705 | |
| H | H | $CO_2CH_3$ | 62 | 3.65 | 1710,1735 | |
| H | $CH_3$ | $CO_2CH_3$ | 60 | 3.65 | 1715,1740 | |
| $CO_2C_2H_5$ | H | $CO_2C_2H_5$ | 58 | 4.11 | 1715,1740 | |
| H | Cl | CN | 50 | | 1710 | 2245 |
| H | $CH_3$ | CN | 50 | | 1705 | 2245 |

In reactions of alkenes 10 with nitrile, ester or ketone substituents, the products 11 are formed in 50-70 % yields. Similar yields are observed in reactions of unsubstituted alkyl radicals$^{5)}$. Therefore, carbonyl substituted radicals 7 behave like nucleophiles$^{7)}$.

Acknowledgement. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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(Received in Germany 15 December 1981)