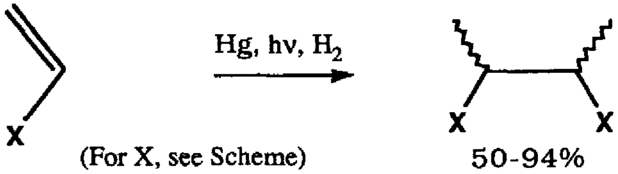
Tetrahedron Letters,Vol.30,No.26,pp 3389-3392,1989   0040-4039/89 $3.00 + .00
Printed in Great Britain   Maxwell Pergamon Macmillan plc

HYDRODIMERIZATION OF UNSATURATED ALCOHOLS, ESTERS, NITRILES, KETONES, AMINES, SILANES, EPOXIDES AND FLUOROCARBONS BY MERCURY-PHOTOSENSITIZATION

Cesar A. Muedas, Richard R. Ferguson, and Robert H. Crabtree*
Sterling Chemistry Laboratory, Yale University
New Haven, Connecticut 06520

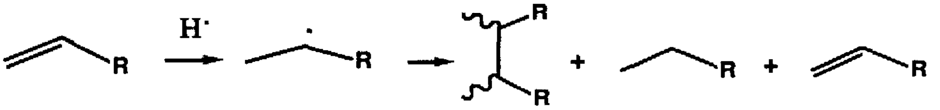
Abstract: Substituted alkenes are efficiently hydrodimerized on a preparative scale in an H_2 atmosphere by Hg(vapor) and 254 nm light.

We report here a new method for the hydrodimerization of alkenes (Eq. 1). An important advantage of this process over the mercury-photosensitized dehydrodimerization of alkanes, ethers, alcohols, and silanes, described previously,[1] is that hydrodimerization tolerates a wider range of functionality on the molecule. The reaction proceeds by initial homolysis of dihydrogen by Hg-photosensitization to give H atoms.[2] Hydrogen atom addition to the alkene generates alkyl radicals which recombine (Eq. 2).[3] The disproportionation products, being volatile, tend to be carried away with the H_2 stream, but the dimer accumulates in the reactor.



(For X, see Scheme)

(1)

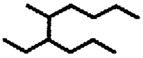
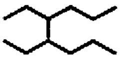


(2)

A second advantage of this method is the enhanced regioselectivity of alkene hydrodimerization compared to the direct reaction of Hg* with alkanes. For example, when 1-hexene is photolyzed under hydrogen, the 2,2'-dimer is by far the major product, especially at short reaction times (see Table, which shows compositions of the dimer fractions). The hydrogen atoms add to alkenes to give the most stable intermediate radical (i.e., $3^{o}>2^{o}>1^{o}$)[4]. With prolonged reaction times, formation of other dimers than the 2,2' can become important. This is because the disproportionation products, hexane and hexenes, build up to some extent in the condensate and then undergo unselective dimerization.

TABLE

Product distribution: hydrodimerization versus dehydrodimerization

					1°-2° dimers
1-hexene $\xrightarrow[H_2]{Hg^*}$	(1 hour)	85%	3%	>1%	11%
	(72 hours)	71%	15%	3%	11%
hexane $\xrightarrow{Hg^*}$		23%	45%	21%	11%

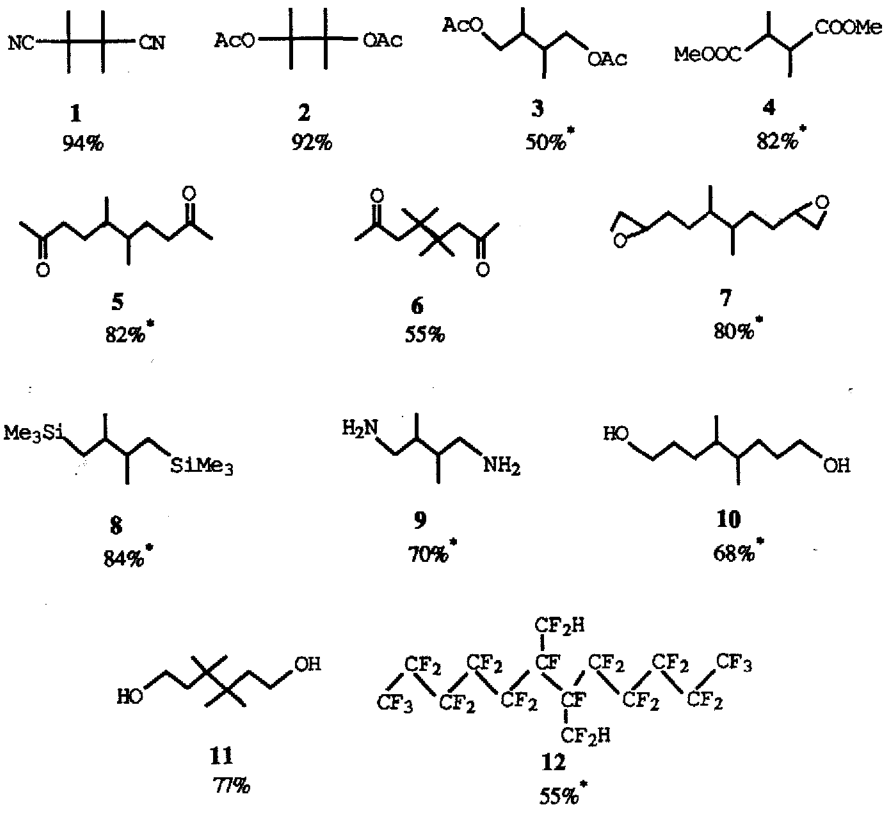
Several functionalities incompatible with simple dehydrodimerization can be introduced as substituents on the alkene that is hydrodimerized.[5] For example, saturated nitriles fail to dehydrodimerize at all, and the direct reaction of most saturated esters and ketones yields very complex product mixtures. However, good yields of the hydrodimerization products are realized when we irradiate the corresponding unsaturated substrates CR'R"=CRX under H_2 according to eqn. 1. Essentially only the dimers from coupling of the most stable radicals are formed. Where meso- and DL- mixtures are possible, both isomers are formed in a nearly 1:1 ratio. Multigram amounts are easily obtained, for example, 1-hexene gives 2.4 mmol of dimeric products per hour (410 mg/h), when a hydrogen stream (30 mL/min) is first saturated with hexene vapor at room temperature and then passed into the lower part of a 1.6 L quartz vessel, containing a drop of Hg, in a 16W Rayonet photoreactor.

Some of the compounds that have been made are shown in the Scheme, together with the fraction of the dimeric products which is the regioisomer depicted. Interestingly, the hydrodimerization that yields **7** proceeds cleanly without fragmentation of the epoxide functionality by Hg*, no doubt because the energy of the Hg* is efficiently channeled into H_2 homolysis.

The effect of the double bond on the regiochemistry of the product is well illustrated by the alcohols **9** and **10**, and the amine **11**. Saturated alcohols[1] and amines[6] are known to dehydrodimerize preferentially at the carbon α to the heteroatom. In contrast, the position where dimerization occurs in the present case is determined by the position of the double bond in the starting material.

Fluorinated olefins are particularly interesting substrates for dehydrodimerization, e.g., **12** is the major product obtained on photolysis of perfluoro-1-heptene, but 1°-2° dimers are also formed (27%).

SCHEME



1 94%

2 92%

3 50%*

4 82%*

5 82%*

6 55%

7 80%*

8 84%*

9 70%*

10 68%*

11 77%

12 55%*

* mixture of stereoisomers

Cross-dimerization is also possible. Cyclohexene and allyltrimethylsilane were chosen because of their similar vapor pressures. The product of the dehydrodimerization of equimolar amounts of these substrates consisted of a ca. 1:2:1 mixture of **8**:1-trimethylsilyl-2-cyclohexylpropane:bicyclohexyl.

The hydrodimerizations are carried out in the photolysis apparatus previously described,[1d,e] with some variations in the general set-up. A stream of H_2 is bubbled through the liquid substrate to saturate the vapor which is then passed into the reactor. The products accumulate by condensation in the quartz reaction vessel as the irradiation proceeds, and are protected from further reaction by their much lower vapor pressure. Volatiles can also be condensed from the exit H_2 stream. As well as starting material, rearranged and hydrogenated products are also found. The amounts of the latter, depending on the substrate and conditions, are typically ca. 10%. The dimers are separated from the crude mixture by distillation or crystallization and are identified by ^{13}C-, ^{1}H-NMR, GC-MS, or comparison with authentic samples.

ACKNOWLEDGMENT.

We thank the Department of Energy for funding, Exxon Corp. for its continued interest and Steve Brown for discussions.

References

(1) (a) Brown S. H.; Crabtree R. H. *J. Chem. Soc., Chem. Commun.* **1987**, 970. (b) Brown, S. H.; Crabtree, R. H. *Tet. Lett.* **1987**, *28*, 5599. (c) Crabtree, R. H. *J. Chem. Ed.* **1988**, *65*, 290. (d) Brown, S. H.; Crabtree, R. H., U. S. Pat. 4,725,342. (e) Brown, S. H.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *111*, 2935, 2946.

(2) First reported in Cario, G.; Frank, J. *Z. Physik* **1922**, *11*, 155.

(3) Cvetanovic, R. J. *Adv. Photochem.* **1963**, *1*, 115, and references cited there.

(4) Early physico-chemical work on photosensitized reactions of hydrogen and lower olefins reported dimer formation from terminal H-addition. Cf. (a) Junger, J. C.; Taylor, H. S. *J. Chem. Phys.* **1938**, *6*, 325.(b) Moore, W. J.; Taylor, H. S. *Ibid.* **1940**, *8*, 504.

(5) Muedas, C. A.; Ferguson, R. R.; Crabtree, R. H., U. S. Pat. Appl., April 11, 1989.

(6) Ferguson, R. R.; Boojamra, C. G. ; Brown, S. H.; Crabtree, R. H. *Heterocycles* **1989**, *28*, 121.

(Received in USA 3 April 1989)