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DEHYDRODIMERIZATION OF KETONES, CARBOXYLIC ACIDS, AMIDES, ESTERS, ALCOHOLS, AND AMINES, VIA MERCURY-PHOTOSENSITIZATION

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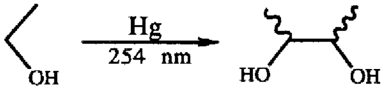
Abstract: Selective dehydrodimerization of the title compounds can be carried out on a preparative scale at 1 atm. and at 25°-110°C in a simple apparatus by Hg-photosensitized reaction under H_2.

A variety of substrates can be conveniently dehydrodimerized (e.g., eqn. 1), under conditions previously described,[1] but these are not suitable for all classes of compounds.



(1)

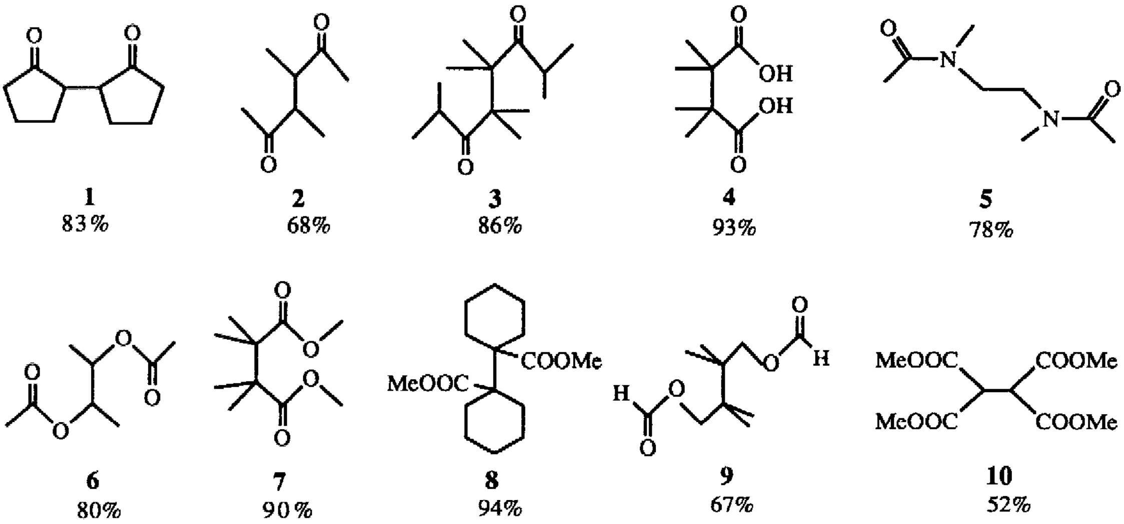
Ketones, esters, carboxylic acids, and amides failed to form dehydrodimers at all. Alcohols and amines did react but often showed poor selectivity. We now report conditions which allow the unsaturated compounds to be dehydrodimerized with high selectivities and yields, and which improve the selectivity of the reaction for the saturated compounds. Multigram quantities of dimers[2] can be obtained over 24 hours.

By running the reaction under H_2 at a temperature sufficiently below the reflux temperature of the substrate so that H_2 is the major constituent of the vapor, we replace ^3P_1Hg (Hg*) by H· as the principal H-atom abstracting reagent.

The photoexcited mercury atom, Hg*, selectively transfers its energy to the H_2. The hydrogen atoms thus generated[3] abstract H from C-H bonds of the substrate,[4] and the resulting carbon centered radicals recombine. As in our earlier work, the dehydrodimer is protected because the low vapor pressure of the dimer prevents it from evaporating and reacting further. The H_2-mediated reactions avoid the undesirable direct interaction of the substrate with Hg*, which fails to lead to dehydrodimer for the unsaturated compounds, or gives lower selectivity for the saturated compounds.

Scheme 1 shows some of the dehydrodimers not obtainable under reflux conditions but only by the new procedure. Scheme 2 shows the effect on selectivity of running the saturated substrates under the new conditions.

Scheme 1 Dehydrodimerization products accessible by the new method [§,2]



1 83%

2 68%

3 86%

4 93%

5 78%

6 80%

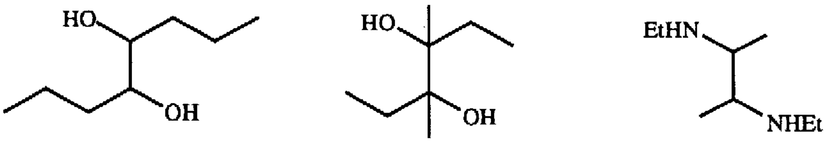
7 90%

8 94%

9 67%

10 52%

Scheme 2 Comparison of selectivity in dehydrodimerizations (abstracting reagent shown in parenthesis)[§,2]



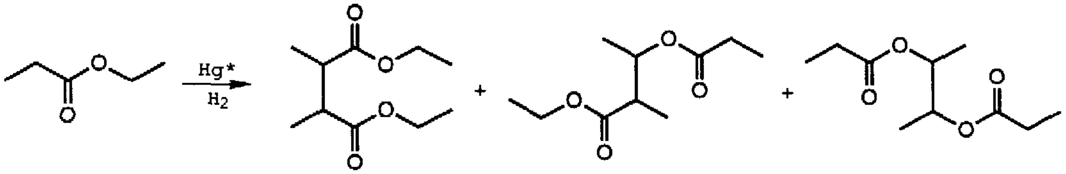
11
53% (Hg*)
87% (H·)

12
88% (Hg*)
95% (H·)

13
40% (Hg*)
90% (H·)

[§] Figures show percentages of the illustrated dimers in the crude mixture after removal of starting material.

The selectivities observed depend on the relative stabilities of the different radicals that can be formed in each case. For example, ketones dimerize α to the carbonyl group with a preference for 3°>2°>1° C-H bonds (**1**-**3**). Dimethylamine was unreactive under the conditions of eqn. 1, but can be dimerized under the new conditions after protection as the N-acetyl derivative (**5**). Esters R'COOR" dimerize α to the -COO- group. If R' and R" are different, selective dimerization occurs at the most substituted α-carbon (**6**-**10**). If R' = R", then there is a preference for reaction α to C over α to O, as shown by the composition of the dimer mixture in eqn. 2.[2] Even free carboxylic acids can be dimerized (**4**).

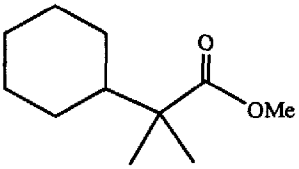


(2)

14 36% **15** 46% **16** 14%

Improved selectivity is observed in the reactions leading to **11**-**13**. For the alcohols, the direct Hg* reaction produces significant attack at β and γ C-H bonds. For the amine, the by-products in the Hg* case were an uncharacterized mixture.

Cross-dimerizations are also possible and afford the expected mixtures[2], e.g., **17** or **18** are obtained, together with bicyclohexyl and **1** or **7**, when cyclopentanone or methyl isobutyrate react with cyclohexane. Methyl isobutyrate also reacts with 2,4-dimethyl-3-pentanone afford a mixture of **19**, **3** and **7**. Varying the ratio of cosubstrates in the vapor phase can also be used here to fine tune the product composition.[5]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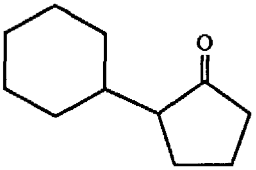
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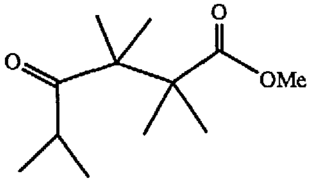
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In every case hydrogen must be more abundant than the organic starting material in the vapor phase so that Hg* interacts primarily with H_2. A hydrogen stream (ca. 20-70 mL/min) at 1 atm is saturated with the substrate and reacts in the photochemical apparatus described in Ref 1.[6] The dehydrodimers were isolated by distillation or crystallization and characterized by ^{1}H- and ^{13}C-NMR, IR, GC-MS, or comparison with authentic samples.

In conclusion, mercury photosensitized dehydrodimerization is now applicable to a much wider range of substrates and can provide better selectivities than previously attained.

Acknowledgement. We thank the Department of Energy for funding.

References and Notes

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.*, **1989**, *111*, 2935, 2946.
2. All possible stereoisomers are formed, e.g., D,L and meso mixtures for each of **1**, **2**, **6**, **7**, **11**, **13**, **14**, and **16**.
3. First reported in Cario, G.; Frank, J. *Z. Physik* **1922**, *11*, 155.
4. Steacie, E. W. R.; *Atomic and Free Radical Reactions*; Reinhold: New York, 1954; v. 1, pp. 410-482 and v. 2, p. 506.
5. Previously discussed for direct cross-dimerizations by Hg*, Cf. Ref. 1e.
6. Depending on the boiling point of the substrate, two typical set-ups are used: (a) The less volatile compounds (b.p. > 120°C) are placed directly in the apparatus[1e] (1.3 L quartz vessel, 16-bulb Rayonet reactor, low pressure Hg-lamps). The reaction vessel is heated to a temperature 30-60° lower than the b.p. of the substrate. H_2 is passed (20-50 mL/min) through the organic substrate via a stainless steel or teflon needle. (b) Compounds with b.p. < 120°C are placed in a 200 mL flask outside the reactor and the system kept at constant temperature 10-50°C below the reflux temperature of the substrate. H_2 is bubbled through the flask and the gas stream transferred via stainless steel or teflon cannula to the lower part of the reaction vessel. In each case, irradiation is carried out for 12-48 hours.

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