

Mercury-photosensitized reactions

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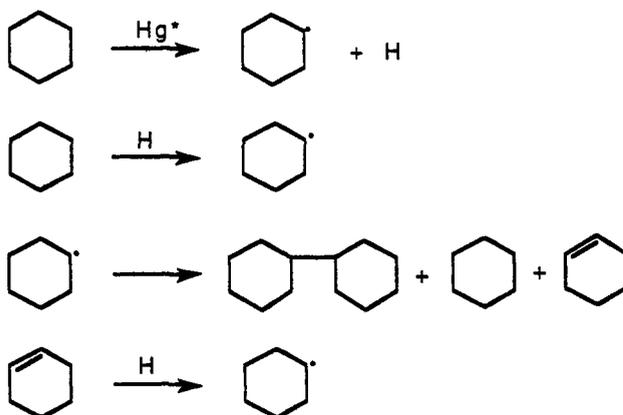
Abstract: Hg Photosensitization reactions have selectivity for volatile molecules which allows partial oxidation of alkanes and selective dehydrodimerization of a wide variety of organic molecules.

Hg photosensitization via the 3P_1 state (Hg^*) allows the dehydrodimerization and functionalization of a variety of volatile organic molecules on a 1 to 50g scale in standard laboratory photochemical equipment at room temperature and pressure. (1-6) The system was initially developed for the functionalization of alkanes on a preparative scale, but it has now been extended to a wide variety of substrates. The substrate is placed in a quartz reactor with a drop of Hg and irradiated with a 254 nm *low-pressure* Hg lamp. The liquid phase is unreactive so when the product condenses it is protected from further reaction. This product protection by vapor pressure selectivity is critical in allowing partial oxidation, normally especially difficult in the case of alkanes where the partial oxidation products are more reactive than the starting alkanes. The origin of the effect seems, at least in part, to be the precise energy matching between the atomic Hg in the emitting lamp and the atomic Hg in the gas phase of the reactor. The spectrum of the Hg in the liquid phase shows the ca. 254 nm line is strongly broadened and shifted, so liquid phase Hg is not an efficient absorber of radiation. Non Hg^* photochemistry is also largely suppressed because most of the radiation is absorbed by Hg.

Hg Photosensitized reactions were very extensively studied (7) in the period 1945-73, but the focus was almost exclusively physicochemical. The use of low pressures meant vapor pressure selectivity effects were not recognized and the studies were largely restricted to simple alkanes which are of relatively limited interest in synthetic organic chemistry. A few synthetic applications of Hg photosensitization have been reported: both triplet sensitization (8) and applications to inorganic synthesis of silanes and germanes (9) were briefly explored.

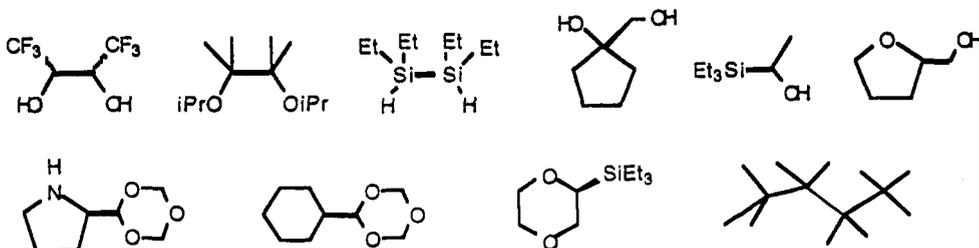
Hg* Conditions Under our standard conditions, with reflux under N_2 (Hg^* conditions), Hg^* is the reactive species which attacks the substrate. C-H bond scission produces C-centered radicals and H atoms. The H atoms do not recombine but tend to abstract H from substrate, fortunately with a selectivity ($3^\circ > 2^\circ > 1^\circ$) very similar to that of Hg^* itself, to give further C-centered radicals. These recombine and disproportionate. The dehydrodimer condenses and is protected from further reaction

but the alkene product of disproportionation, which normally complicates the product mixture in conventional radical reactions, remains in the vapour and is rapidly converted back into C-centered radicals by attack of H atoms. Any alkene formed is therefore rapidly recycled into the radical pool. These reactions are shown for cyclohexane in Scheme 1. In an effort to find a lower limit of volatility needed to undergo the reaction, we successfully dimerized $n\text{-C}_{18}\text{H}_{38}$ at 200° in vacuo or with steam distillation at 100°C .



Scheme 1 Pathways Proposed for Cyclohexane

Extension to alcohols, ethers and certain amines proved possible and a broad series of compounds can be conveniently synthesized by the dimerization procedure. Typical examples are shown in Scheme 2, where the new bond formed is marked in bold. For alcohols, ethers and amines, high selectivity for attack at a C-H bond α to a heteroatom is observed. In cases where two different substances react, the two homodimers and the heterodimer are all formed. This can be synthetically useful because the three compounds are often sufficiently different in polarity and volatility to be easily separable.



Scheme 2 Some Compounds Formed under Hg^* Conditions

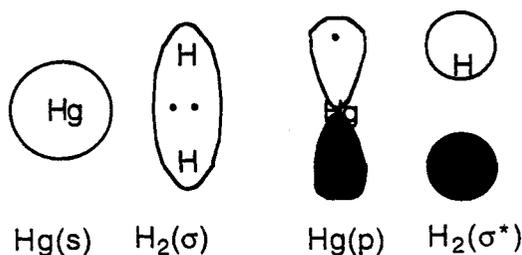
Trioxan is an interesting cosubstrate in these studies because it gives a protected aldehyde as product. For example, the cross-dimer from trioxan and cyclohexane gives $\text{C}_6\text{H}_{11}\text{CHO}$ on hydrolysis. The overall process is equivalent to an alkane carbonylation. Another example shown in the Scheme is a protected form of prolinal, formed from trioxan and pyrrolidine.

Detailed study of the mixed substrate systems shows that the reactivity of a given bond depends on its strength and on the volatility of the substrate in question. Where bond strengths are known, we can estimate the product ratio to be expected. Where the bond strengths are now known, we can estimate them using an equation that originally appeared in patents by Cier. (10) In cases such as $n\text{-}$

octane, in which a large number of C-H bonds of similar strength are present, attack is observed at all 2° C-H bonds, and statistical recombination of the radicals takes place. The resulting materials have a very low freezing point for their M.Wt., a feature which may lead to practical applications.

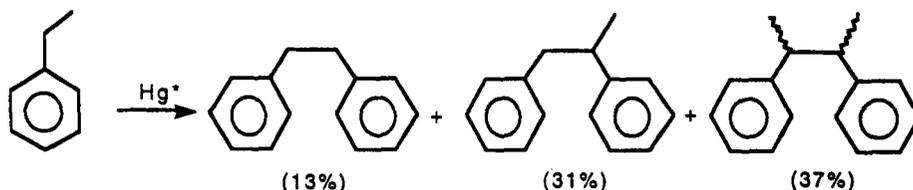
The alkane-derived radicals can also be trapped by neutral molecules such as CO, SO₂ or O₂. In the CO case, we find that R₂CO is the major product formed. For SO₂ a mixture of species is obtained, but oxidation produces the sulfonic acid, RSO₃H, in good yield. (6a) Oxygen gives the hydroperoxide, ROOH. (6b)

Exciplex Formation and Hg^{*}/H₂ Conditions The Hg^{*} conditions fail for certain substrates if the Hg^{*} attacks a functional group, rather than a C-H bond. This seems to happen because Hg^{*} has a stronger affinity for lone pairs and π-bonds than for σ-bonds, as is suggested by the studies of Breckenridge, Soep et al. (11) Hg^{*} has an s¹p¹ electronic configuration and so a lone pair donor such as NH₃ can bind via a 2e bond, nominally of half-order. The Hg^{*}-NH₃ binding energy of 17 kcal/mol is consistent with this idea. By analogy with transition metal cleavage, Scheme 2 shows how the transfer of one electron from H₂(σ) to the Hg s orbital, combined with one electron transfer from the Hg s orbital to H₂(σ^{*}) could lead to a reduction of the H-H bond order to zero. (12)



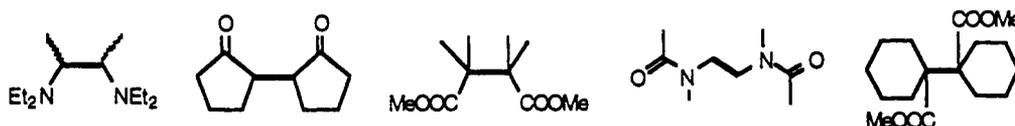
Scheme 3 How Hg^{*} may Split Covalent Bonds.

Typical examples of substrates that behave poorly under Hg^{*} conditions are ketones, esters, carboxylic acids and most amines. Arenes are interesting in that cleavage of the weak benzylic C-C bond is a significant pathway under these conditions. This suggests that the Hg^{*} may bind to the arene ring in a π-fashion and transfer its energy to the molecule as a whole, but the problem is not yet fully resolved.



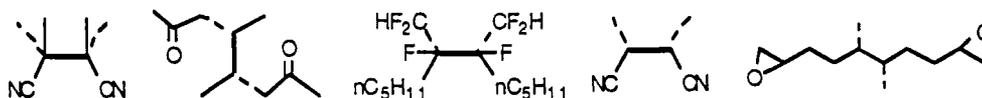
In many cases, the presence of a reactive atmosphere, either H₂ (Hg^{*}/H₂ conditions) (4) is useful for preventing direct attack by Hg^{*} on the substrate. Under optimal conditions, when p(H₂) is about 660 mmHg and p(substrate) is about 100 mmHg, H₂ is far more reactive than the substrate. H atoms now take over from Hg^{*} as the active abstractor. The presence of lone pairs or π-bonds in the substrate apparently does not interfere significantly and a much wider range of substrates can now be

dehydrodimerized. For example, NEt_3 fails to react at all under Hg^* conditions, presumably because Hg^* attacks the N lone pair and energy transfer leads to thermal excitation of the substrate but not to productive chemistry. Under Hg^*/H_2 conditions, probably because H atom addition leads to undesired and unselective partial saturation of the aromatic ring. Scheme 3 shows some of the compounds that can be formed in this way. Quantum yields of 0.04-0.8 are usual and the majority of substrates have values in the range 0.2-0.6. Chemical yields are good to excellent (40% to 98%).



Scheme 4 Some Dehydrodimerization Products formed under Hg^*/H_2 Conditions

The proposed attack of H atoms on alkene C=C bonds (Scheme 1) suggested that it might be possible to use Hg^*/H_2 conditions to convert alkenes. This proved very successful, as shown in Scheme 5, where the dotted bond shows the site of the original C=C bond and the bold line represents the new C-C bond. By choosing the position of the double bond in the substrate it was possible to form a radical center at a defined location along a chain and so make a defined compound rather than a mixture.



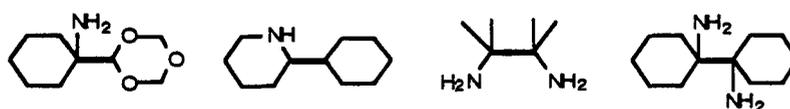
Scheme 5 Some Hydrodimerization Products formed under Hg^*/H_2 Conditions

It was possible to use the $\text{Hg}^*/\text{H}_2/\text{alkene}$ method to identify the mixture of products formed from saturated analogues. For example, under Hg^* conditions, n-butanol forms the α,α -, α,β -, and α,γ -dimers, but authentic samples were not readily available for comparison. We therefore looked at a series of Hg^*/H_2 reactions; for example, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH}$ alone gave γ,γ -dimer, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$ gave β,β -, $\beta\gamma$ -, and γ,γ -dimer, and $\text{CH}_3\text{CH}_2\text{CH}=\text{CHOMe}$ gave α,α -, α,β -, and β,β -dimer. This and related experiments allowed identification of all the dimers. (13)

An interesting case shown in the Scheme is that of fluoroalkenes, $\text{R}_1\text{CF}=\text{CF}_2$. These add H at the terminal position and the resulting dimer is the 2,2'-isomer. The terminal H substituents are clearly identifiable in the ^1H NMR of the product, confirming the mechanistic proposal for the reaction.

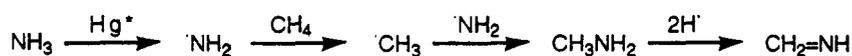
In addition to the expected hydrodimer, t-BuCH=CH₂ also gave a small amount of material derived from a 1,2-methyl migration in the intermediate radical. This type of rearrangement does not usually take place in radicals, but the ones formed in this case have a large amount (ca. 40 kcal/mol) of excess thermal energy that is slow to dissipate in the vapor. If this were the origin of the rearrangement, it should be suppressed by addition of a powerful quencher of vibrational energy, such as CO_2 . Experimentally, we found a significant quenching effect which seems to confirm the proposal. Another typical radical reaction is addition to C=C double bonds. This cannot be very efficient in the

Scheme 7 shows some compounds that have been synthesized by the Hg^*/NH_3 route.

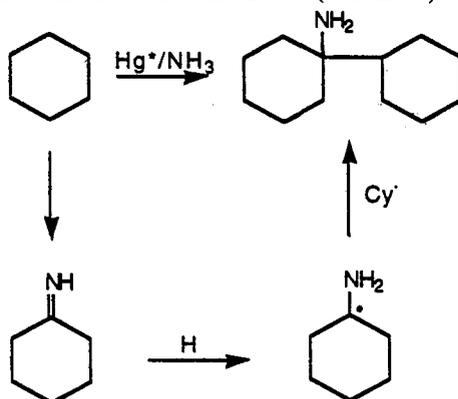


Scheme 7 Some Compounds formed under Hg^*/NH_3 Conditions

Methane, having a C-H bondstrength of 105 kcal/mol., does not react well under Hg^*/NH_3 conditions, an involatile oil, containing C, H and N is formed. We imagined that this might be the result of the thermal oligomerization of an intermediate imine such as $\text{CH}_2=\text{NH}$. To avoid the problem, we felt we needed to trap the initial products and developed a reactor (5a) in which the gases were rapidly recycled by a peristaltic pump through a cold trap at -20°C . This allowed trapping of the intermediate, which proved to be $\text{CH}_2=\text{NH}$. This is a known product of the Hg photosensitized reaction of CH_3NH_2 and is probably formed by the following route.



Slowing the gas recycle rate allowed subsequent reactions of $\text{CH}_2=\text{NH}$ to take place. These gave rise to C_2 and C_3 imines. The origin of these species is probably formation of CH_2NH_2 by H atom attack on $\dot{\text{C}}\text{H}_2\text{NH}$, followed by recombination with $\dot{\text{C}}\text{H}_3$, formed from methane. The final result is oligomerization and functionalization of methane. The key role of the ammonia is to catalyze energy transfer from Hg^* to methane. Few reactive gases are available for this purpose because they have to meet strict conditions. They must bind well to Hg^* and have a bond energy of less than 112 kcal/mol. (the energy of Hg^*) to be subject to bond scission. NH_3 has a bond energy of 107 kcal/mol. and is known to bind strongly to Hg^* . (11) The mediator must have a bond strength greater than that of the substrate otherwise the fragments produced will not have the driving force necessary to abstract H from methane; again NH_3 meets this criterion. Other alkanes also react. The major amine product from cyclohexyl is the interesting 3° amine shown. This probably results from recombination of cyclohexyl with the radical derived from H atom addition to the imine (Scheme 8).



Scheme 8 Cyclohexane Amination under Hg^*/NH_3 Conditions

Conclusion This work has suggests that vapor pressure selectivity and other phase-specific reactions might be useful to give selectivities not possible by conventional means. The method makes reactive radicals like H atoms available in preparatively useful amounts using only inexpensive apparatus. Alkanes can be functionalized in a variety of ways. A number of unusual compounds are also available in this way from a variety of alcohols, alkenes, amines, carboxylic acids, ethers, and fluorocarbons. Some are beginning to find applications in other fields, such as monomer synthesis in polymer chemistry. (15)

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