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FUNCTIONALIZATION OF NITROGEN AND OXYGEN CONTAINING HETEROCYCLES BY MERCURY PHOTOSENSITIZED DEHYDRODIMERIZATIONS¶

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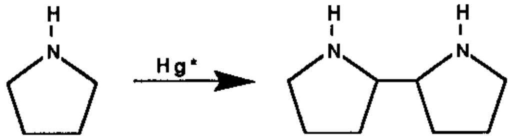
Abstract - Nitrogen and oxygen containing heterocycles can be functionalized by mercury photosensitization.

Mercury photosensitized dehydrodimerization[1] has recently been shown to be a synthetically useful procedure[2]. The homo and cross coupling of compounds such as alcohols, ethers, alkanes, and silanes for example, has yielded many interesting directly functionalized compounds obtained only with comparative difficulty by more conventional methods. For example, methanol and cyclohexane yield cyclohexylmethanol (eq. 1), which is easily separable from the accompanying homo-dimers, thanks to the large polarity differences involved. The substrates are refluxed with a drop of mercury in a quartz reactor. Irradiation of the vapor phase with 254 nm light yields involatile dimers, which condense and return to the bulk liquid and are protected from further reaction, the Hg* reactions being much slower in the liquid phase. The setup is described in more detail elsewhere[2c-d].

$$CH_3OH + C_6H_{12} \xrightarrow{Hg^*} HOCH_2CH_2OH + C_6H_{11}CH_2OH + C_6H_{11}\text{-}C_6H_{11} \qquad (1)$$

We now find that amines display a similar reactivity pattern to their oxygen containing

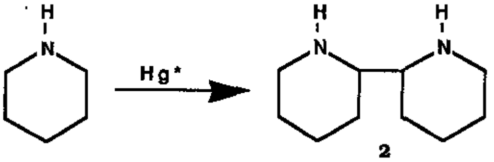


1

dl, meso

(2)

¶ *Dedicated to Professor Sir Derek Barton on His Seventieth Birthday*



(3)

2

dl, meso

analogues. Hg* reaction of amines is especially efficient in the case of cyclic amines. For example, pyrrolidine dimerizes to give **1** (eq. 2). New C-C bonds are formed α to the heteroatomic nitrogen atom. Piperidine yields **2** (eq. 3). Both compounds react to high conversion and yield (Table 1),

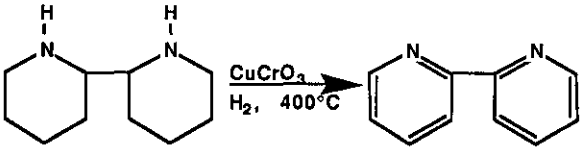
Table 1[a]

STARTING MATERIAL	MONOMER CONVERSION (μMOLES h^{-1})	YIELD OF 2,2'-DIMER
Pyrrolidine	2600	93%[b]
Piperidine	9500	94%[b]

[a] Reaction cond.: 1.5 L quartz tube, 128 W low pressure photoreactor, reflux

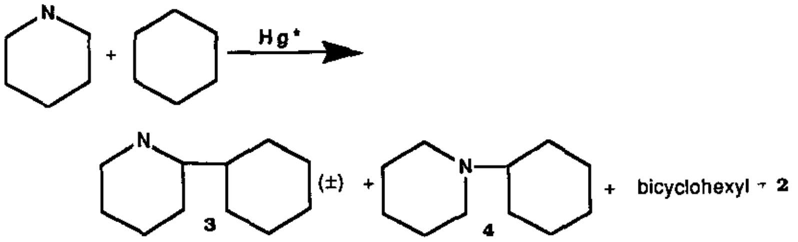
[b] Yield is higher at lower temperature, but at expense of conversion.

and the dimers have potential use as chelating diamines. By passing **2** over copper chromite catalyst in hydrogen at 400°C[3], we obtained 2,2'-bipyridyl (71% conversion, after one pass) and in high yield (>90%) (eq. 4).



(4)

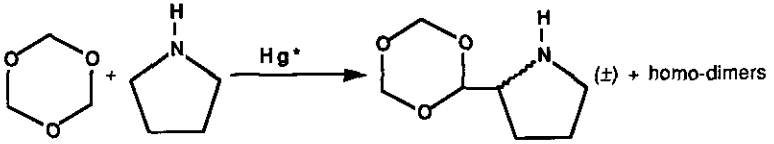
It is also possible to cross couple amines with other classes of compounds, to the same high conversion and yield. For example, the reaction of pyrrolidine and cyclohexane yields **3** and **4** (eq. 5)[4], compounds not previously obtainable in one step from such simple methods[5-6]. The cross-dimers are easily separable from the accompanying homo-dimers. The amine dimers are removed by washing with water, and the cross-dimers are then extracted from the organic phase with dilute acid. **3** and **4** can be separated by column chromatography. Piperidine and



(5)

cyclohexane react similarly to produce the analogous cross-products.

Cyclic ethers such as THF, *p*-dioxane, and *s*-trioxane also react in an analogous way. So, for example, *s*-trioxane can be cross-dimerized with pyrrolidine to give the prolinal derivative shown in eq. 6, a light yellow oil smelling of corn chips, as the cross dimer in 40% yield. (^{13}C nmr: 92.7, CH_2O; 103.2, CHO; 59.6, CHNH; 46.2, CH_2NH; 24.8 and 25.6, β-CH_2 groups of pyrrolidine ring.)



(6)

A notable feature of equations 5 and 6 is that they are also alkane functionalization reactions. Alkane C-H activation is an area of current interest[7]. The reaction proceeds by C-H bond homolysis followed by recombination of radicals. Alkene products of radical disproportionation are not seen because they are scavenged by H atoms formed during the initial C-H bond cleavage[2d].

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4. Cyclohexane (75 g), piperidine (25 g), and a drop of mercury were placed in a 1.5 liter quartz flask. The liquid was brought to reflux under Ar. The vapor phase was photolyzed for 21h in the photoreactor of ref 2c, containing sixteen 8-watt low pressure mercury lamps. The reagents were evaporated, leaving 13.8 g of involatile dehydrodimers. The molar ratio of **2** :**4** :bicyclohexyl:**3** was 1:3.5 :9:9.5. The ratio depends on the mole ratio of reagents in the and therefore on the liquid compostion and the temperature of the system[2d].
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