

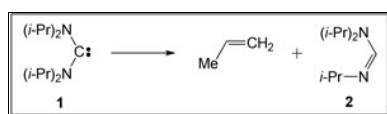
# Noteworthy Chemistry

October 1, 2012

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**The Alder carbene decomposes at room temperature.** R. W. Alder and co-workers described acyclic diaminocarbenes 16 years ago (*Angew. Chem., Int. Ed.* **1996**, 35, 1121–1123). These compounds have greater nucleophilicity, basicity, and  $\sigma$ -donating ability than N-heterocyclic carbenes. Other authors described them as indefinitely stable at room temperature in solution and the solid state and inert toward small molecules such as  $\text{NH}_3$  and CO.

U. Siemeling and coauthors at the University of Kassel and Goethe University Frankfurt (both in Germany) examined the stability claims and report the thermal decomposition of the “Alder carbene” [bis(diisopropylamino)carbene, **1**]. They stored the carbene in a solution of toluene- $d_8$  and, using  $^1\text{H}$  NMR spectroscopy, observed that it decomposed after several days. To exclude an intermolecular reaction with the toluene methyl group, they used benzene- $d_6$  instead, but the decomposition persisted. The products were propylene and *N,N,N'*-triisopropylformamidine (**2**). The decomposition is a concentration-independent, intramolecular process.



The authors used density functional theory to study the fragmentation mechanism. The results indicated that the reaction is strongly exergonic ( $\Delta G^\circ = -22.7$  kcal/mol). The low activation barrier ( $\Delta G^\ddagger = 27.8$  kcal/mol) indicates that the reaction is probably concerted.

A similar study of an asymmetric piperidinocarbene showed that intramolecular fragmentations are not limited to **1**. The authors conclude that the reactivity and synthetic potential of this class of compounds is underestimated. (*Chem.*

*Commun.* **2012**, 48, [9123–9125](#); [José C. Barros](#))

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**“Missing” tropospheric organic acids may have been found.** Organic acids appear in significant amounts in the troposphere; an estimated 60–120 t form each year. Current atmospheric models, however, fail to predict the origin of as much of half of the amount of organic acids generated.

While investigating the photochemistry of MeCHO in the atmosphere, D. U. Andrews, B. R. Heazlewood, and co-workers at the University of Sydney developed a detailed kinetic model that identified the crucial role played by keto–enol phototautomerization in organic acid formation. Traditional models predict that MeCHO photolyzes with a quantum yield of 14%. The remainder is assumed to cool by collision processes.

The authors used laser photolysis in a helium supersonic expansion medium to confirm the reported photolysis quantum yield based on a collision-free model. More importantly, they found that keto–enol isomerization readily occurs under UV irradiation at 310–330 nm. In addition, when collisions at atmospheric pressure are considered, a quantitative model predicts a quantum yield of  $21 \pm 4\%$  for the formation of vinyl alcohol from keto–enol phototautomerization. Because vinyl alcohol is a known organic acid precursor, these results may help account for “missing” organic acids. (*Science* **2012**, 337, [1203–1206](#); [Xin Su](#))

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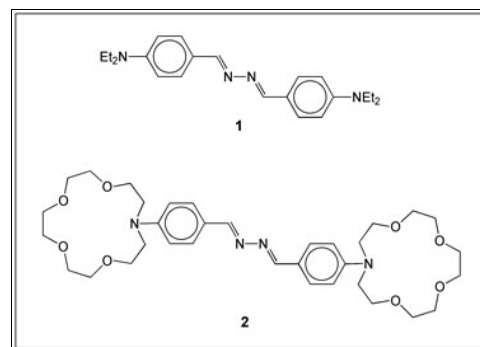
**Luminescence behavior is dictated by molecular interactions.** Several molecular rotors exhibit aggregation-induced emission (AIE): the nonemissive molecules are induced to emit light by forming them into aggregates. Many research groups have tried to understand how AIE works, but the complicated mechanisms remain unclear.

In an effort to understand the role of molecular interaction in an AIE process, a team led by H. Zhou at Anhui University (Hefei, China) synthesized a series of dibenzylidenehydrazine derivatives (e.g., **1** and **2** in the figure) and studied their crystal structures and fluorescence properties.

Although the structures are similar, the two molecules behave very differently. Compound **2** is AIE active, but **1** is not. The crystal structures reveal that there is no molecular interaction in **1** to prevent the flexible N–N bond from rotating. Its free twisting makes it nonluminescent in the solid state and therefore AIE inactive.

In sharp contrast, strong molecular interactions in the crystal structure of **2** fix the N–N single bond and inhibit its twisting motion. As a result, it has a pronounced AIE effect. (*J. Mater. Chem.* **2012**, 22, [16927–16932](#); [Ben Zhong Tang](#))

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**Tailor phase separation in organic photovoltaics.** R. Verduzco and a team of researchers at Rice University (Houston), Argonne National Laboratory (IL), and the University of Chicago used supramolecular interactions to synthesize conjugated block copolymers (BCPs) and develop a route to all-polymer organic photovoltaics. They used ureidopyrimidone (UPy) to promote self-complementary coupling between three conjugated polymers and two coil polymers to generate the BCP blends. The conjugated polymers were poly(3-hexylthiophene) (P3HT), poly(9,9-dioctylfluorene) (PFO), and poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (PFBT). The coils were poly(ethylene glycol) and polystyrene.

The degrees of phase separation and individual block crystallization in the conjugated supramolecular BCPs can be controlled by changing the annealing temperature and/or introducing solvents. The BCPs’ thin-film morphologies illustrate the crucial interplay between BCP architecture, block characteristics, and UPy coupling.

The authors also examined the fluorescence behavior of P3HT–PFO and P3HT–PFBT supramolecular donor–acceptor blends. Compared with donor–acceptor blend controls, the decreased separation distances mediated by UPy associations increased fluorescence quenching. These initial studies highlight the potential of supramolecular interactions for mediating transport and performance in energy devices. (*Macromolecules* **2012**, 45, [6571–6579](#); [LaShanda Korley](#))

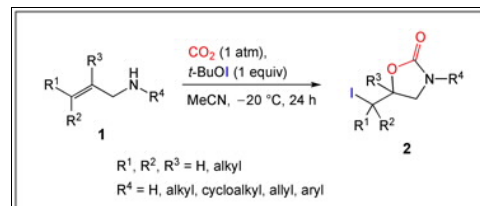
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**Use atmospheric carbon dioxide to make cyclic carbamates.** Because climate change is closely linked to the increasing level of CO<sub>2</sub> in the atmosphere, there is a growing interest in finding new ways to reduce atmospheric CO<sub>2</sub>. One way is CO<sub>2</sub> capture and utilization; however, because of the stability of CO<sub>2</sub>, this tactic often requires harsh conditions.

S. Minakata and co-workers at Osaka University (Japan) were intrigued by the reaction of *tert*-butyl hypoiodite (*t*-BuOI) with atmospheric CO<sub>2</sub> and allyl alcohol to form a cyclic carbonate. But the reaction requires excess *t*-BuOI because the equilibrium does not favor cyclic carbonate formation. The authors decided to use allylamines instead of allyl alcohols. After optimization, they obtained series of cyclic carbamates (see figure) in high yields from various functionalized allylamines and only 1 equiv of *t*-BuOI.

The reaction also gave good yields with gem-disubstituted 2-propynylamines. The resulting cyclic carbamates bear an iodine atom, a good leaving group, which makes them good candidates for synthetic intermediates. The reaction also works well with homoallylamines and substituted propargylamines. (*Org. Lett.* **2012**, *14*, **4874–4877**; [Chaya Pooput](#)) [*The authors claim to remove CO<sub>2</sub> ( $\approx 3.3 \times 10^{-4}$  atm partial pressure) from the atmosphere, but all of the examples in the article use a full 1 atm of CO<sub>2</sub>.—Ed.*]

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**Take efficient, green routes to receptor antagonist precursors.** Ethyl 5-methyl-1,2,4-oxadiazole-3-carboxylate and 4-iodo-1-methylpyrazole are key building blocks for synthesizing a somatostatin receptor antagonist. This compound may be useful for treating type 2 diabetes, depression, and anxiety. R. T. Ruck and co-workers at Merck (Rahway, NJ, and Hoddesdon, UK) report a one-pot synthesis of the oxadiazole starting from ethyl cyanofornate.

The cyanofornate is treated with NaOAc and NH<sub>2</sub>OH·HCl in HOAc. The intermediate amidoxime is acetylated by adding Ac<sub>2</sub>O, and the cyclization is achieved by heating at 99 °C to generate the oxadiazole in 95% yield.

The iodination of 1-methylpyrazole is carried out with 0.6 equiv H<sub>2</sub>O<sub>2</sub> and 0.5 equiv I<sub>2</sub> to give 4-iodo-1-methylpyrazole in 91% yield. The only byproduct is water. (*Org. Process Res. Dev.* **2012**, *16*, **1329–1337**; [Will Watson](#))

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