

Entomocorticum fungal food source. The beetle deals with the aggressive fungus by harboring yet another species—an actinomycete bacterium—that secretes antibiotics to kill *O. minus*.

This coleopteran complexity eluded detection until now, even though *D. frontalis*, first described 140 years ago (4), is a widespread pest and arguably the most economically important pest of southern pine plantations in the United States. And it is by no means unique in harboring a complex microcosm of interacting species. *Acromyrmex* leaf-cutting ants associate with two very specialized symbiotic basidiomycete fungi that grow in underground gardens as food. At the same time, these ants maintain actinomycete *Pseudonocardia* bacteria on their cuticle to manufacture antibiotics that inhibit the growth of an unwelcome associate—*Escovopsis*, a parasitic fungus that attacks the food-source fungal garden (5). As Scott *et al.* suggest, in view of the enormous selection pressure that pathogens can exert, protective associations with antibiotic-producing bacteria may be a ubiquitous feature of insect-fungus partnerships. Given that more than 300,000 species of beetles are currently known, the number of partnerships, fungal associates, and bacterial symbionts yet to be elucidated is daunting.

According to May (6), the reasons for cataloging biodiversity are the “same reasons that compel us to reach out toward understanding the origins and eventual fate of the universe, or the structure of the elementary particles that it is built from.” May

also reminds us that Earth’s biodiversity is declining at an unprecedented rate, due in large part to anthropogenic changes in land use, climate, soil, and water and air quality. How many beetles, with their communities of associates, will have ceased to exist before Scott *et al.* and other investigators can work out the details of their interrelationships is anyone’s guess. According to the Red List of Threatened Species provided by the International Union for Conservation of Nature (7)—an authoritative accounting of rare, threatened, and endangered species—fewer than 800 of the 950,000 or so species of insects that have been described (~0.1%) have been evaluated as to their status. Moreover, of the insect species that have been evaluated, almost three-fourths are threatened. The powerful antibiotic chemistry exploited by the southern pine beetle that allows it to go about its business attacking trees is just one example of a more tangible benefit of examining terrestrial interactions than simply gaining insights into the cosmos.

There is no limit to what remains to be discovered in that interactive zone between macroorganism and microbe, where so many biological mutualisms and antagonisms play out. Microbes blanket the planet, and in their infinite variety they must be involved in infinite interactions. Deciphering these could lead to a vast increase in ecological knowledge, as well as to the isolation of natural products of unforeseen function. The latter possibility, clearly envisioned by Scott *et al.*,

is one that we take to be of particular importance. Chemical prospecting—the search for chemicals of use from nature, including medicinals—has been relegated to low priority by industry nowadays, in the belief that nature has already been exhaustively screened for such compounds. Scott *et al.* provide proof that such belief is unjustified, that the microbial world has been all but thoroughly explored (see the figure). Sure enough, microbes have been screened for some types of biotic and antibiotic action, but the bulk of their chemical capabilities remain to be uncovered. As demonstrated by Scott *et al.*, even the least wanted among species can be the source of useful leads. A concerted effort to look into the more subtle aspects of microbial chemistry is therefore very much in order. The fact is that we don’t even know the microbes themselves that inhabit our planet, let alone the molecules they need to secure their survival. Microbial ecology is still very much a part of the great frontier.

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10.1126/science.1164873

ATMOSPHERIC SCIENCE

From Ocean to Stratosphere

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The increasing burden of greenhouse gases from human activities, such as carbon dioxide, is warming the troposphere (the lowest part of Earth’s atmosphere), whereas in the stratosphere (above the troposphere and extending from ~16 to 50 km), higher greenhouse gas concentrations cause a net radiative cooling that may delay ozone hole recovery in the Antarctic. But the picture is even more complex. Recent studies have shed light on how mass exchange between troposphere and stratosphere may be affected by

tropical sea surface temperatures (SSTs) that are rising as a result of global warming.

The mass exchange between troposphere and stratosphere—the Brewer-Dobson circulation—is characterized by persistent upwelling of air in the tropics from the troposphere into the stratosphere. The air then downwells in the extratropics, mixing stratospheric air back into the troposphere, with a turnaround time of a few years (1). Some observational data indicate that the troposphere-stratosphere mass exchange is accelerating (2). Most numerical studies with coupled chemistry-climate models support this finding and relate it to the anthropogenic climate signal (3), but it is uncertain which

Rising tropical sea surface temperatures alter atmospheric dynamics at heights of 16 kilometers or more.

mechanism communicates the anthropogenic climate signal to the mass exchange.

This mechanism needs to be pinpointed because the troposphere-stratosphere mass exchange affects the chemical composition and climate of Earth’s atmosphere. The tropical upwelling branch of the Brewer-Dobson circulation lowers temperatures and ozone concentrations, especially in the lower stratosphere. The low temperatures in turn freeze-dry the upwelling tropospheric air. Furthermore, the upwelling controls the lifetime of anthropogenic ozone-depleting substances with sinks in the stratosphere. In the extratropical stratosphere, downwelling causes adiabatic warming and ozone accumulation until

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the air parcels return to the extratropical troposphere. This process contributes tropospheric ozone levels (4). Finally, changes in horizontal temperature gradients in the lower stratosphere cause remote shifts in surface weather and climate (5).

Evidence for a changing Brewer-Dobson circulation comes from satellite and radiosonde data, which indicate a reduction in temperatures and ozone and water vapor concentrations over the past four decades, partic-

The model studies indicate that the upwelling intensification is mainly induced by a stronger driving from planetary waves; one to three troughs of these global-scale waves fit around a whole latitude circle. Planetary waves are produced in the troposphere by various processes, and can travel horizontally as well as vertically. Their life cycle usually ends when they disintegrate as a result of continuous damping or, more abruptly, due to wave breaking (like water waves approaching a

the subtropical upper troposphere and lower stratosphere. These stronger winds are caused by the growing temperature contrast between the lower stratosphere, which cools, and the tropical upper troposphere, which warms, as a result of anthropogenic climate change. The altered zonal winds intensify planetary-wave disintegration in the stratosphere at low latitudes, thereby accelerating the tropical upwelling (10, 13, 17).

The warming of the tropical upper troposphere is mainly caused by higher tropical SSTs, which are part of global warming. The SST increase intensifies the activity of tropical thunderstorms (see the figure), which strengthens the associated latent-heat release, warms the tropical upper troposphere, and thus accelerates the zonal winds. However, it remains unclear whether altered wave generation or propagation dominate this SST-governed impact on the Brewer-Dobson circulation and whether waves generated in the tropics or extratropics are involved.

To address these open questions, an additional SST-related mechanism is being considered. The latent heat release from tropical thunderstorms causes pressure perturbations and hence generates tropical planetary waves, just like a stone hitting a water surface (9, 15, 18). The impact of this mechanism on the Brewer-Dobson circulation could strengthen as tropical SSTs rise and wave generation increases (19). In particular, observations show that SSTs in the western tropical Pacific Ocean—the highest



Tropical oceans and thunderstorms. Warmer tropical oceans intensify the activity of tropical thunderstorms, such as the “Hector” thunderstorm that develops nearly every year off the islands to the west of Darwin, Australia. As a result, the release of latent heat strengthens, affecting planetary waves and hence the mass exchange between troposphere and stratosphere.

ularly in the tropical lower stratosphere at all longitudes (6). This points to an accelerated tropical upwelling (2, 7). Radiative changes as a result of anthropogenic ozone depletion might account for similar modifications (8), but cannot explain a sudden drop in tropical lower stratospheric temperatures in 2001 (2, 7). Stratospheric mass transport trends derived from observations also tend to indicate accelerated upwelling but have large uncertainties (7, 9).

Several independent studies with numerical global climate models confirm these observations (3, 10–13). Consistently, the model studies find that lower temperatures and ozone concentrations occur in the tropical lower stratosphere as a result of a stronger tropical upwelling in a future warmer climate, although the high-latitude Brewer-Dobson response differs among the studies.

Some planetary waves can enter the stratosphere, where they usually vanish, conveying energy and momentum to the Brewer-Dobson circulation (14). During their life cycle, planetary waves are susceptible to SSTs, which affect location and intensity of their disintegration patterns.

Simulations show that there are various different latitudes where stratospheric wave disintegration responds to SST modifications (10, 12). However, theoretical considerations imply that any year-round intensification in tropical upwelling requires enhanced stratospheric wave disintegration in the tropical/subtropical region (15, 16). The key question is how this low-latitude disintegration enhancement relates to higher tropical SSTs.

As an explanation, some model studies highlight the role of stronger zonal winds in

SSTs on Earth—are anticorrelated with temperatures and ozone and water vapor concentrations in the tropical lower stratosphere (2). For example, high-SST anomalies coincide with low temperatures and ozone concentrations, and vice versa. The anticorrelation could be communicated via planetary-wave generation by tropical thunderstorms, as explained above (6).

Thus, heat and moisture at the sea surface affect not only tropospheric climate but also stratospheric dynamics. In particular, planetary waves appear to communicate modulations in tropical SSTs to the mass exchange between troposphere and stratosphere. This Brewer-Dobson circulation is likely to intensify in a future climate with higher tropical SSTs, with implications not only for the chemical composition and climate of the stratosphere but also at Earth’s surface.

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- We thank H. Huntrieser for helpful comments. Further thanks go to R. Garcia, W. Randel, and F. Wu for sending their manuscripts.

10.1126/science.1163799

CHEMISTRY

A Light Touch Catalyzes Asymmetric Carbon-Carbon Bond Formation

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One of the most formidable tasks in organic synthesis is the formation of carbon-carbon bonds, in part because the activation of the carbon atoms requires the control of highly reactive species. Not only must these reactions form the correct bond connectivity, but they usually need to produce one enantiomer (the left- or right-handed arrangement of functional groups around each carbon atom that acts as a stereogenic center). The α -alkylation of carbonyl compounds (those containing a C=O group) with alkyl halides is a classical method, but it works much better for ketones (two alkyl groups on the C=O) than for aldehydes (one alkyl and one H on the C=O) and often requires stoichiometric amounts of additional reagents to direct the handedness at the stereocenter. On page 77 of this issue, Nicewicz and MacMillan report a remarkable approach for the enantioselective α -alkylation of aldehydes that not only is catalytic but uses a photoredox cycle to control the formation of highly reactive intermediates (1).

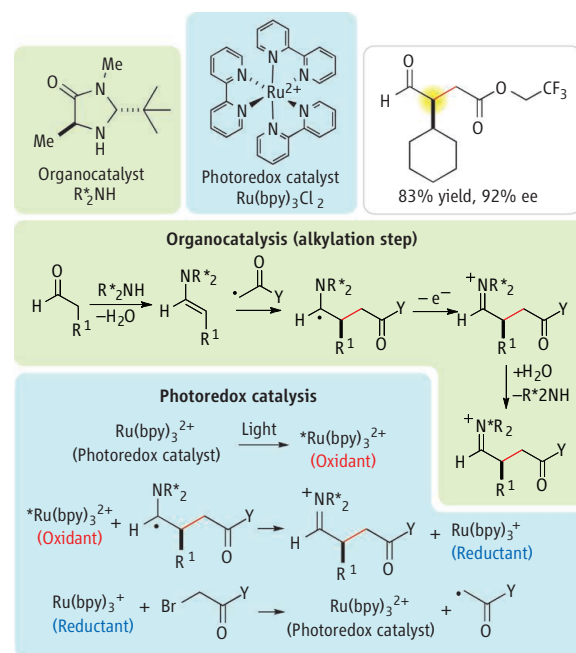
Prior to this work, asymmetric versions of these α -alkylation reactions that yield preferentially one enantiomer relied heavily on the use of chiral auxiliaries, which help direct the stereochemistry of the product (2). However, chiral auxiliaries, in contrast to catalysts, are used in stoichiometric amounts, and additional steps are required for their attachment and removal. These considerations alone render the chiral auxiliary approach unsuitable for large-scale applications. Consequently, the development of catalytic systems that gener-

ate enantiomerically pure compounds by using a minimal amount of an environmentally friendly catalyst is a field of intensive research (3).

Given that aldehydes are among the most widely used building blocks in organic synthesis, α -alkylation reactions of aldehydes that are both catalytic and enantioselective would be highly desirable. Despite extensive efforts, such reactions have remained elusive until recently (4). The problem is that alkyl halides are only modestly reactive toward nucleophiles (reagents that form a new chemical bond by donating both bonding electrons), which necessitates the use of highly reactive aldehyde enolates. Because aldehyde enolates are difficult to prepare and are expected to react faster with the starting aldehydes than with an alkyl halide, a truly catalytic cycle is nearly impossible to achieve.

Nicewicz and MacMillan have proposed a solution to this challenging problem in which the difficult and slow ionic alkylation step (a two-electron process) has been replaced by rapid steps based on less stable open-shell molecules involving one-electron pathways. MacMillan's and Sibi's groups had already introduced the concept of organo-SOMO catalysis (one-electron processes that

The cooperation between a photoactivated catalyst and an organocatalyst enables a so far elusive stereoselective synthetic transformation.



Asymmetric catalysis via one-electron steps. The steps of the organocatalytic reaction (green shading) are carefully intertwined with the photoredox cycle of Ru(bpy)₃²⁺ (blue shading). The photoexcited state of Ru(bpy)₃²⁺ readily oxidizes the radical resulting from the coupling of the activated alkyl halide and the enamine, which is generated by condensation of the aldehyde with the organocatalyst. The bulky chiral organocatalyst directs the approach of these reactants so that alkyl group R¹ has a preferred stereochemistry; hydrolysis recovers the final product. The photocatalyst, now Ru(bpy)₃⁺, reduces the alkyl halide by one electron to create the radical (the activated species with an odd electron) as well as the initial Ru(bpy)₃²⁺. (Upper right) A typical product, its yield, and enantiomeric excess (ee).

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