

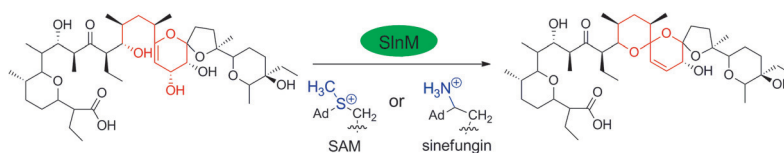
## Biosynthesis



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Formation of the  $\Delta^{18,19}$  Double Bond and  
Bis(spiroacetal) in Salinomycin Is  
Atypically Catalyzed by SlnM,  
a Methyltransferase-like Enzyme



**Think positive:** By using S-adenosylmethionine (SAM) or sinefungin (a methylation inhibitor) as a cofactor, SlnM, a methyltransferase homologue, was shown to catalyze the spirocyclization-

coupled dehydration of C19 in salinomycin biosynthesis. SAM, or more specifically its positive charge, has been considered to be essential in the enzymatic conversion.

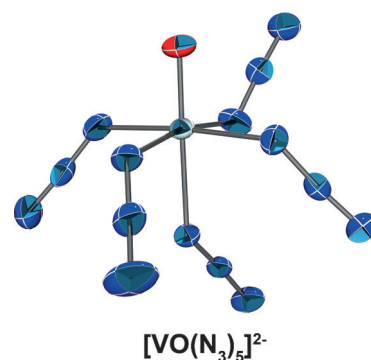
## Vanadium Oxoazides

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The Vanadium(V) Oxoazides  $[\text{VO}(\text{N}_3)_3]$ ,  
 $[(\text{bipy})\text{VO}(\text{N}_3)_3]$ , and  $[\text{VO}(\text{N}_3)_5]^{2-}$

**Handle with care:** Vanadium(V) oxoazides were prepared and characterized for the first time.  $[\text{VO}(\text{N}_3)_3]$  was obtained from  $[\text{VOF}_3]$  and  $\text{Me}_3\text{SiN}_3$  as a very friction- and impact-sensitive solid. The reaction of  $[\text{VO}(\text{N}_3)_3]$  with 2,2'-bipyridine and  $[\text{PPh}_4]\text{N}_3$  afforded  $[(\text{bipy})\text{VO}(\text{N}_3)_3]$  and  $[\text{PPh}_4]_2[\text{VO}(\text{N}_3)_5]$ , respectively, which were characterized by single-crystal X-ray structure determination.



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# Flashback: 50 Years Ago ...

The field of organic semiconductors is a hot topic today, and 50 years ago the area was already attracting some interest as scientists were keen to know whether organic compounds showed similar behavior to the better known inorganic semiconductors. In a Review, Hans Meier discussed the photoconduction properties of organic dyes, including n- and p-type conductivity. Polythiophenes, cyanine dyes, and phthalocyanine derivatives were among the compounds described.

Carrying out experiments in liquid hydrogen fluoride is certainly not for the faint hearted, however studies on the reaction of liquid hydrogen fluoride (which is a stronger acid than its aqueous counterpart) with nitrous acid and its

derivatives were indeed carried out, as outlined in a Review by Fritz Seel. The products of these reactions contained nitrosyl fluoride solvated by hydrogen fluoride, and are valuable reagents in fluorine chemistry.

André S. Dreiding reported on a rearrangement of *ar*-tetralols. When 1,2,3,4,6,9-hexahydro-6-oxo-9-methylnaphthalene was heated with sulfuric acid, 8-methyl-5-tetralol was the major product, and when mineral acids were used then 5-methyl-7-tetralol was the major product. However, with 70 % perchloric acid, 7-methyl-5-tetralol was the sole product. The differences were ascribed to the reactions being either under kinetic or thermodynamic control. Dreiding was the founder of the famous

Bürgenstock Conference, which celebrated its 50th anniversary this year (for more details see *Angew. Chem. Int. Ed.* **2015**, 54, 5014).

Ekkehart Winterfeldt published a Communication on the stereochemistry of the addition reactions to acetylenic triple bonds. Mechanistic studies showed that the *cis* adducts are produced by a cyclic electron shift, and contradicted previous claims that compounds with easily abstractable hydrogen atoms always undergo *trans* addition reactions. Winterfeldt's Obituary can be read at *Angew. Chem. Int. Ed.* **2015**, 54, 35.

[Read more in Issue 8/1965.](#)