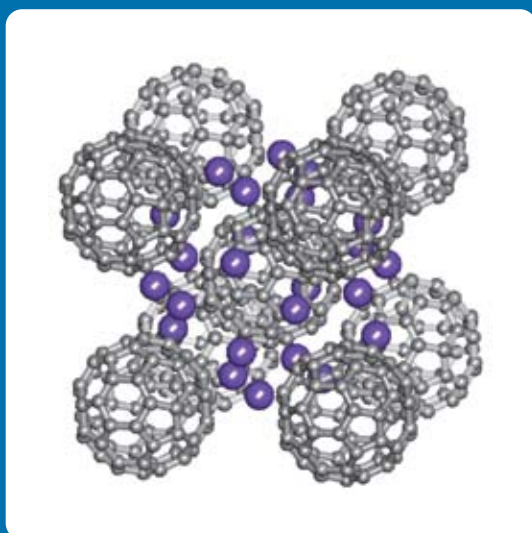


# TCIMAIL

number **165**



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## Compounds Composed of Two Elements (2)

Kentaro Sato

Carbon atoms can assemble into various types of stable molecular skeletons, while they are also capable of forming strong bonds with many other elements. Because of these properties, the combination of carbon and just one other element can create an extremely diverse chemical space. In the previous article we focused on halocarbons, so this time let us take a glance of compounds composed of carbon and metallic elements, and carbon and oxygen.

### Carbon and Metallic Elements

You can imagine all sorts of compounds based on the combination of carbon and a metallic element. In terms of substances consisting of only the two elements, metal alloys like steel can be included in the same category.

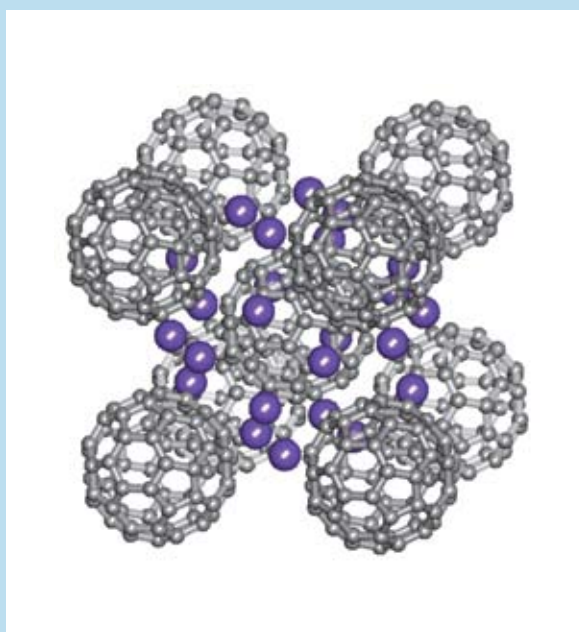
A famous compound made of a metal and carbon is calcium carbide ( $\text{CaC}_2$ ). It exists as a relatively stable solid, and since it reacts with water to produce acetylene, it has long been used as a fuel source. Other metals such as sodium and copper form similar acetylides and compounds like  $\text{Li}_4\text{C}_3$  and  $\text{Mg}_2\text{C}_3$ , which are called sesquicarbides, are also known.

There are almost completely unrelated types of compounds too. For example, there are compounds called intercalation compounds, in which metal ions are inserted into the space between the stacked layers of graphite.  $\text{KC}_8$ , a typical example, contains potassium ions between the sheets of graphite and is produced by treating graphite with potassium vapor at a very high temperature. The strongly reducing property of  $\text{KC}_8$  is often used for purposes such as the formation of multiple bonds between heavy elements.

Graphite intercalation compounds containing alkali and alkaline earth metals other than potassium are known.

Some of them show superconductivity as exemplified by  $\text{CaC}_6$ , which is drawing an attention for becoming a superconductor at a relatively high transition temperature of 11.5 K.

When it comes to superconductivity, however, fullerenes “doped” with metallic elements such as potassium are probably more well-known. In 1991, a compound with the composition  $\text{K}_3\text{C}_{60}$  was discovered to exhibit superconductivity at a remarkably high temperature of 33 K and received a considerable attention as a case demonstrating special possibilities of fullerenes. At present, the fullerene doped with cesium ( $\text{Cs}_3\text{C}_{60}$ ) under pressurized conditions holds the record for the highest transition temperature for molecular superconductors (38 K).

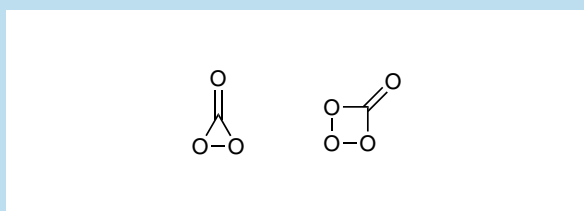


An image of fullerene  $\text{K}_3\text{C}_{60}$  doped with potassium.

### Compounds Composed of Carbon and Oxygen

In organic compounds, oxygen is the second most important partner of carbon only behind hydrogen. Then, from just carbon and oxygen, how many oxocarbon compounds do you think exist or can be synthesized? The first ones that come to your mind are probably simple oxides such as carbon monoxide and carbon dioxide.

Besides CO and CO<sub>2</sub>, carbon trioxide and carbon tetroxide are actually known. But of course, these are very unstable species that were only detected as transient intermediates during the reaction of CO<sub>2</sub> and O<sub>2</sub> under electric discharge conditions.



Carbon trioxide (left, one of possible structures) and carbon tetroxide (right).

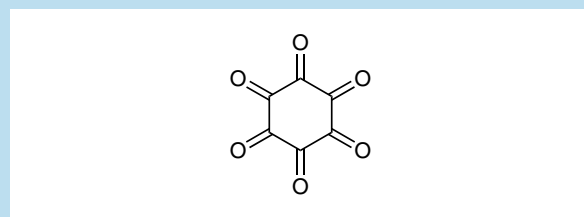
A compound called carbon suboxide (or tricarbon dioxide) is also known. This atypical compound has a structure of O=C=C=C=O in which the five atoms are straightly aligned, and it can be considered as a dehydrated form of malonic acid. It is a gas with a noxious odor that polymerizes easily by external stimuli such as light.

An even longer oxocarbon compound, tetracarbon dioxide (O=C=C=C=C=O), was synthesized by Maier in 1990, and this one is also known to be very unstable. Pentacarbon dioxide (O=C=C=C=C=C=O) was also synthesized by Maier in 1988. Interestingly, though it is prone to polymerization when isolated, it is stable enough to be stored at room temperature as a solution.

A shorter sibling of this family, ethylenedione (O=C=C=O), has never been synthesized or even detected to this day. It is probably one of the simplest yet untouched organic compounds. These oxocarbons have very simple structures consisting of only carbon and oxygen atoms connected linearly, but as is often the case, predicting their physical properties is not as simple.

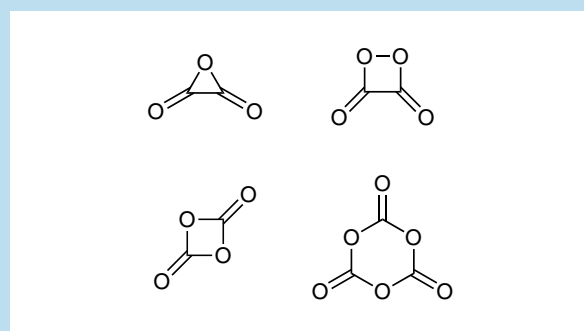
Cyclic compounds consisting of (CO)<sub>n</sub> units are another simple but interesting oxocarbons. Compounds with n=3 to 6 have been known, but they decompose easily to carbon monoxide and have been detected only minutely by mass spectrometry.

Among these, cyclohexanehexone (n=6) is also known as triquinoyl and commercially available as a reagent. But it is isolated in hydrated forms, so its actual shape is more like dodecahydroxycyclohexane.

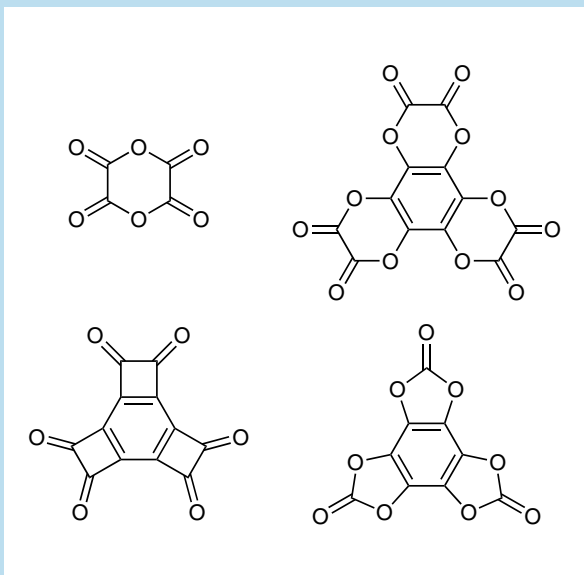


Cyclohexanehexone (triquinoyl)

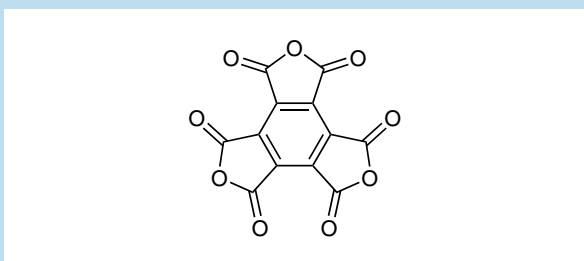
In addition to the compounds mentioned thus far, you could come up with many more structural possibilities on paper. However, most of them would be either synthetically inaccessible or too unstable to exist for a meaningful period of time. For instance, the group of compounds shown below has never been synthesized. Even if they were synthesized, it is easy to imagine that they would fall apart quickly into carbon monoxide or carbon dioxide.



There are compounds that have been synthesized but were either extremely short-lived or only detected to exist analytically (e.g. by NMR). Shown below are the examples of those.



An example of stable oxocarbon compounds is mellitic anhydride, which is a triply dehydrated form of benzenehexacarboxylic acid (mellitic acid) having the molecular formula of  $C_{12}O_9$ . This is actually a historically venerable compound, with its discovery dating back to 1830 and the discoverers being Justus von Liebig and Friedrich Wöhler, who were two of the founding fathers of organic chemistry. Rather unexpectedly, it was isolated from a mineral ore called mellite. Mellite is a rare rock whose major constituent turns out to be the aluminum salt of mellitic acid, so it makes sense that the rock was the source of this oxocarbon compound.



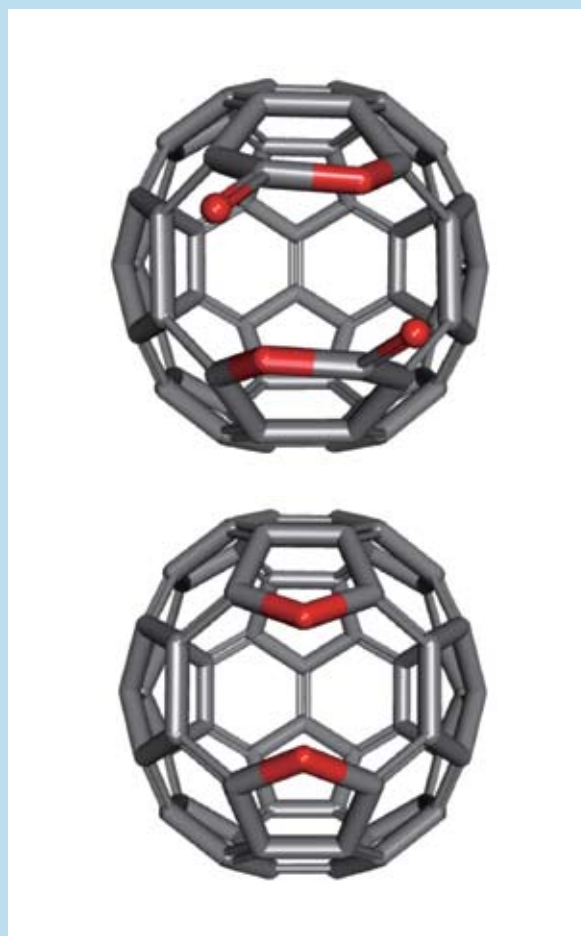
Mellitic anhydride

### Oxides of Nanocarbons

The chemistry of oxocarbons became more and more diverse after 1990's with the advent of the age of nanocarbons. The oxides of these new carbon allotropes began to appear in journals one after another.

Fullerene  $C_{60}$ , for example, can be epoxidized to  $C_{60}O$  using appropriate oxidizing agents, and this epoxide is an important intermediate to synthesize various fullerene derivatives. Depending on the oxidation conditions, the polyepoxides such as  $C_{60}O_2$  and  $C_{60}O_3$  are also produced, and the isomers of  $C_{70}O$  are known as well. Moreover, other interesting fullerene oxides, such as  $C_{120}$  in which two buckyballs are linked by an oxolane ring, have been synthesized.

In 2012, the bis-lactone derivative of fullerene  $C_{60}O_4$  with a "cage-opened" shape was synthesized. Additionally, further derivatives have been detected by mass spectroscopy including the oxafullerene  $C_{58}O_2$ , which corresponds to  $C_{60}O_4$  minus two molecules of carbon monoxide. Oxocarbon compounds derived from fullerene are likely to continue to expand.



Fullerene bis-lactone  $C_{60}O_4$  (top) and oxafullerene  $C_{58}O_2$  (bottom).

One of the materials that have attracted an attention recently is graphene oxide. It can be obtained by oxidizing graphite with potassium permanganate or similar reagents. Surprisingly, it was discovered half a century before graphene itself.

Because graphene oxide is thought to contain oxygen atoms not only as epoxides but also as aldehydes and carboxylic acids, it is not precisely a compound composed of *only* carbon and oxygen. Nevertheless, it has an interesting property that its electric conductivity can be tuned by changing the degree of oxidation, which has led to a growing expectation that it could be a great material for things like electrodes.

As we have gone over, the breadth of compounds made of only carbon and oxygen atoms can be impressive indeed. In my next column, let us move on to the realm of compounds based on carbon and nitrogen.

#### Introduction of the author :

##### **Kentaro Sato**

[Brief career history] He was born in Ibaraki, Japan, in 1970. 1995 M. Sc. Graduate School of Science and Engineering, Tokyo Institute of Technology. 1995-2007 Researcher in a pharmaceutical company. 2008-Present Freelance science writer. 2009-2012 Project assistant professor of the graduate school of Science, the University of Tokyo. 2014-present Publicist for  $\pi$ -system figuration, scientific research on innovative areas.

[Specialty] Organic chemistry

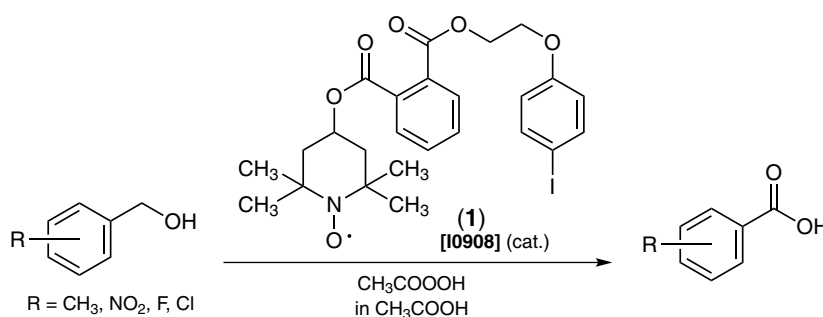
[Website] The Museum of Organic Chemistry <<http://www.org-chem.org/yuuki/MOC.html>>

## Hybrid-type Oxidizing Catalyst Using Peracetic Acid as a Co-oxidizing Agent

**10908** 4-[2-[2-(4-Iodophenoxy)ethoxy]carbonyl]benzoyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl (**1**)

100mg

Yakura *et al.* have reported the synthesis of a new organic hybrid-type catalyst 4-[2-[2-(4-iodophenoxy)-ethoxy]carbonyl]benzoyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl (**1**) and its use for the oxidation reaction of primary alcohols. **1** consists of a 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) group and an iodophenyl group bound together by a covalent bond with the TEMPO moiety of it acting as a oxidizing catalyst of alcohols while the iodophenyl moiety of it also acts as a precursor of an iodobenzenediacetate oxidizing agent. Because of this structure, primary alcohols are oxidized to the corresponding carboxylic acids by the addition of a catalytic amount of **1** with the co-oxidant of peracetic acid. This oxidative reaction is environmentally benign because peracetic acid is transformed into acetic acid after completion of the oxidation.



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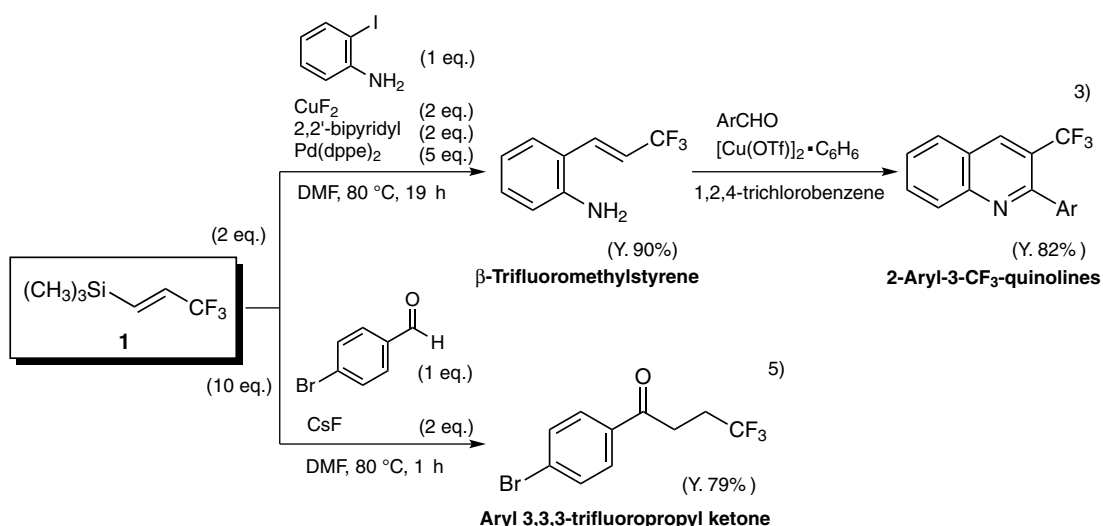
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## A New 3,3,3-trifluoropropenylation Reagent, Ikeda–Omote Reagent

T2977 (E)-Trimethyl(3,3,3-trifluoro-1-propenyl)silane (1)

1g, 5g

$\beta$ -Trifluoromethylpropenylbenzene derivatives have been reported as useful compounds for liquid crystal and organic electroluminescence materials.<sup>1)</sup> (E)-Trimethyl(3,3,3-trifluoro-1-propenyl)silane (Ikeda–Omote Reagent) (1) is a new 3,3,3-trifluoropropenylation reagent, developed by Omote *et al.* 1 effectively participates in a Hiyama cross-coupling reaction with aryl iodide to construct  $\beta$ -trifluoromethylstyrene in good to excellent yields.<sup>2-4)</sup> The styrene derivative provides 2-aryl-3-trifluoromethyl-quinolines, which may make an important contribution to drug discovery.<sup>3,4)</sup> In addition, the reaction of 1 with arylaldehydes in the presence of CsF affords aryl 3,3,3-trifluoropropyl ketones.<sup>5)</sup>

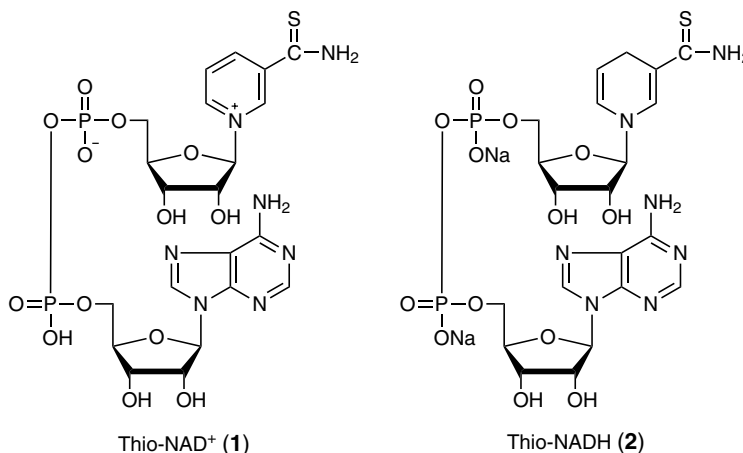


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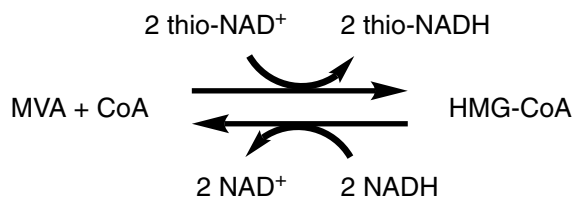
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## Redox Coenzymes

T2979	Thionicotinamide Adenine Dinucleotide oxidized form (1)	100mg
T2980	Thionicotinamide Adenine Dinucleotide Disodium Salt reduced form (2)	100mg



Enzymatic cycling methods have been designed for amplifying sensitivity to assay a small amount of substrate or enzyme activity.<sup>1)</sup> Earlier studies on enzymatic cycling methods were described on DAN<sup>+</sup>, NADP<sup>+</sup>, and CoA.<sup>2-4)</sup> Thio-NAD<sup>+</sup> (1) contributed to improvement of the enzymatic cycling method.<sup>1,5-8)</sup>



Conversion of MVA to HMG-CoA by HMG-CoA reductase<sup>6)</sup>

An example of application of 1 for the enzymatic cycling method is shown above. As 1 is converted to thio-NADH (2) by such an enzymatic reaction, the reaction can be traced by the production of 2. Accumulation of 2 can be monitored by the increase in its absorbance (400 nm), which is at a longer wavelength than NADH (340nm).<sup>8)</sup> On the other hand, 2 was also applied for analysis of the active form of bleomycin.<sup>9)</sup>

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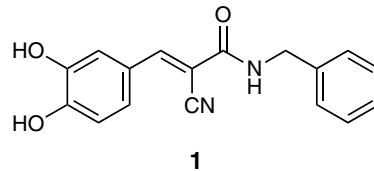
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## JAK Inhibitor

T2962 Tyrphostin AG490 (1)

20mg, 100mg, 1g



The Janus kinase (JAK) family is one non-receptor tyrosine kinase. Each protein has a kinase domain and a catalytically inactive pseudo-kinase domain, and each binds the cytokine receptor through FERM domains.<sup>1)</sup> JAKs are activated on the binding of cytokines to their receptors.<sup>1,2)</sup> The activated JAKs phosphorylate the receptors, creating docking sites for signaling molecules, STAT (signal transducer and activator of transcription) family.<sup>2)</sup>

Tyrphostin AG490 (1) is an inhibitor of EGFR (epidermal growth factor receptor) tyrosine kinase.<sup>3)</sup> 1 has been shown to inhibit activation of JAK2 in pre-B ALL (acute lymphoblastic leukemia) cells.<sup>4)</sup> 1 also inhibits JAK3/STAT, JAK3/AP-1, and JAK3/MAPK signaling pathways and blocks JAK3 autophosphorylation.<sup>5-7)</sup>

FERM domain: domains found in molecules such as Band 4.1, ezrin, radaxin, and moesin.

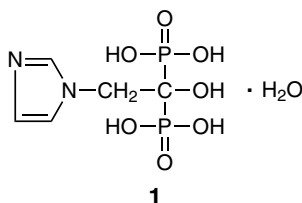
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## Bone Resorption Inhibitor

Z0031 Zoledronic Acid Monohydrate (1)

1g, 5g



Zoledronic acid (**1**) is a bisphosphonate (BP), which inhibits bone resorption, and is classified as a third-generation heterocyclic nitrogen-containing BP.<sup>1,2</sup> The third-generation BPs inhibit farnesyl pyrophosphate synthetase.<sup>2</sup> As well as other BPs, **1** binds to the calcium phosphate bone mineral hydroxyapatite with high affinity and, when compared with other BPs *in vitro*, **1** has the highest affinity for hydroxyapatite (**1** > alendronate > ibandronate > risedronate > etidronate > clodronate).<sup>3</sup> **1** has been used in the treatment of osteoporosis,<sup>4</sup> Paget's disease,<sup>5</sup> and hypercalcemia of malignancy.<sup>6</sup>

This product is for research purpose only.

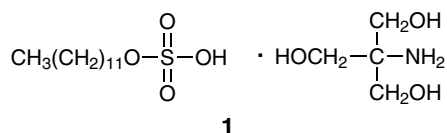
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## Detergent for Biochemical Research

T3071 Tris Dodecyl Sulfate (1)

250mg, 1g



Tris dodecyl sulfate (**1**) is one of the anionic detergents which contains dodecyl sulfate. The property of **1** is different from that of sodium dodecyl sulfate (SDS). **1** has several advantages for biochemical analysis over SDS as described below.

Booth reported that, on two-dimensional electrophoresis of membrane proteins, **1** gives good resolution.<sup>1)</sup> Kubo and Takagi reported the effect of alkanolammonium dodecyl sulfates for Weber and Osborn's polyacrylamide gel electrophoresis system.<sup>2)</sup> The abilities of the dodecyl sulfates as to the dissociation of the molecular assemblies of chlorophyll-proteins were found to decrease in the following order: **1** > triethanolammonium salt > trisopropanolammonium salt.

Depending upon antigens and antibodies, **1** gives different reactivities from SDS on immunoblotting.<sup>3)</sup> **1** was also utilized for chromatographical separation of rat tail tendon collagen from monomeric components.<sup>4)</sup>

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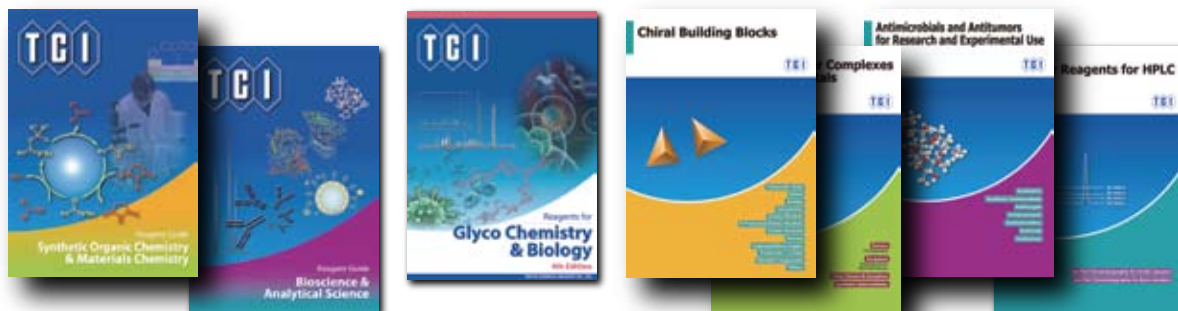
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