

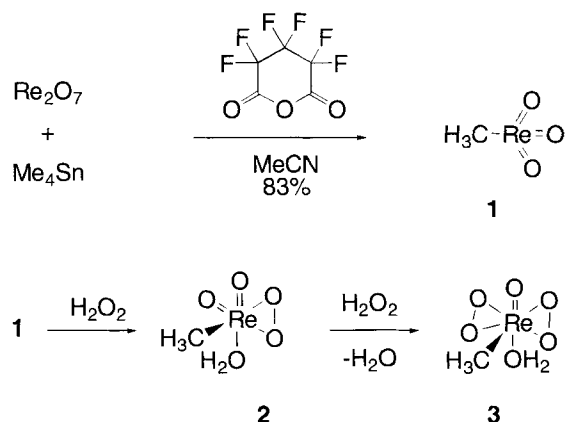
Methyltrioxorhenium – From Oxidation and Cyclopropanation to Metathesis

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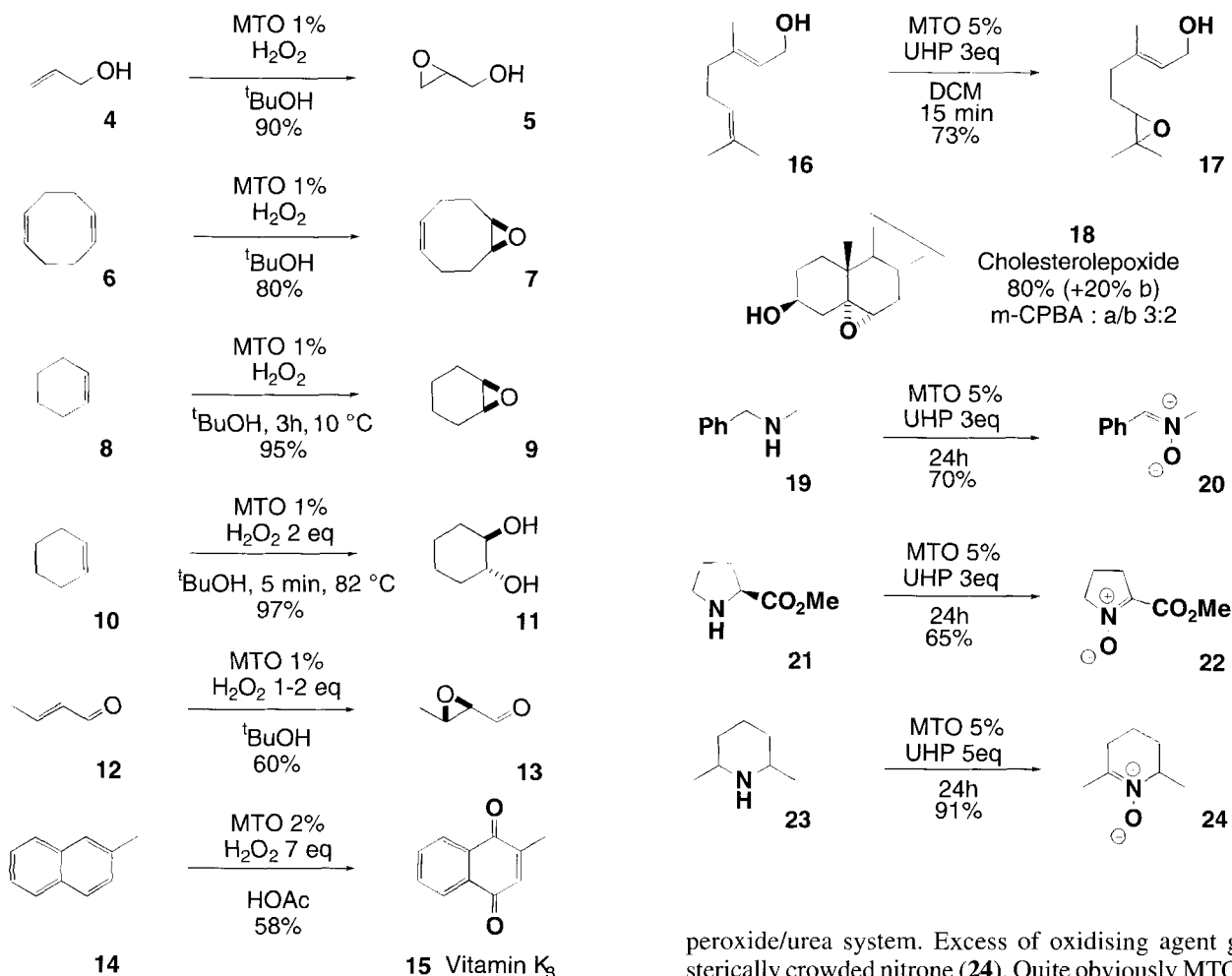
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Metathesis catalysts prepared from Re_2O_7 and tetraalkyltin have been in use for many years. They are used to transform propene, unsaturated carboxylic acids and unsaturated nitriles into more desirable olefins. When Herrmann published the synthesis of new trioxorhenium organyls from 1988 onwards, these Re-d⁰ oxides had immediate impact on organic synthesis. The simplest in this series: methylrheniumtrioxide [MTO], first reported by Beattie, turned out to be most promising. It features an excellent stability against air, moisture, strong oxidants and tolerates even weak aqueous acids and bases (the solubility in H_2O is 50 g/l). It is thermostable (*m.p.* 106 °C) and dissolves readily in most organic solvents. Just strong acids or bases cause decomposition by liberation of CH_4 . Usually stability is a drawback, not an advantage, when it comes to catalytic activity, but not so in the case of methylrheniumtrioxide! The generation of MTO (**1**) from Re_2O_7 and tetramethyltin was soon improved by additional hexafluoroglutaric anhydride, which almost doubled the yield. But yields and synthesis are no longer worrisome, as MTO is commercially available by Sigma-Aldrich and Fluka.



The Oxidations

The reaction of MTO with hydrogen peroxide gives stable η^2 -peroxo complexes (**2**, **3**), which are the active 16 electron catalysts in the olefin epoxidation by H_2O_2 . The butterfly rhenium bisdioxirane (**3**) reacts with olefins even at $-25\text{ }^\circ\text{C}$ within minutes, making MTO one of the most active oxidation catalysts known. This reaction is limited to hydrogen peroxide as oxygen donor, as *tert*-butylhydroperoxide, di-*tert*-butylperoxide and peracids do not react with MTO. For all practical purposes the catalytic oxidation is run at an H_2O_2 :olefin: MTO-ratio of 150:120:1 in solvents like *tert*-BuOH, THF and toluene. Reactions conducted at 10–25 °C for up to 10 h give the epoxides (**5**, **7**, **9**) in good to excellent yields. The electron deficient croton aldehyde (**12**) gives the epoxide (**13**) in just 60% yield. If the exothermic reaction is run at $>70\text{ }^\circ\text{C}$ for a few minutes, the epoxides will be opened to form the *trans*-diols (**11**). The latter reaction is mediated by a Brønsted acid. The system likens the epoxidation by peracids, *e.g.* *meta*-chloroperbenzoic acid, but offers easier work-up. Excess hydrogen peroxide is destroyed by catalytic MnO_2 . Filtration and removal of the solvent leaves the crude products, which are purified by distillation or crystallisation. This procedure was used to oxidise 2-methylnaphthalin to vitamin K_3 (**15**) without the usual amounts of toxic chromic by-products. The MTO/ H_2O_2 system turned out to be the superior reagent for the mono-epoxidation of [60]fullerene. Ethylbenzene, on the other hand, is a poor substrate, which is oxidised to a whole range of products. The comparatively slow oxidation (10–72 h) of saturated hydrocarbons by MTO and H_2O_2 at 40–80 °C gave three products: ketones, alcohols and predominantly hydroperoxides, but the process lacks in yield and selectivity unless 3°-hydrogens are involved. In this case, the oxidation occurs with retention of configuration. The reaction time can be shortened to 6 h by addition of pyrazine-2-carboxylic acid, yet the still slow reaction rate makes this process unfeasible for functionalised substrates, as the oxidation of most functionalities will occur significantly faster.

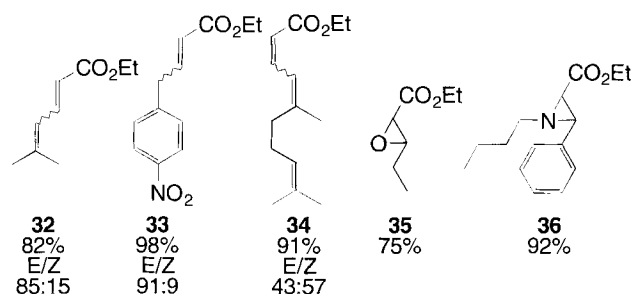
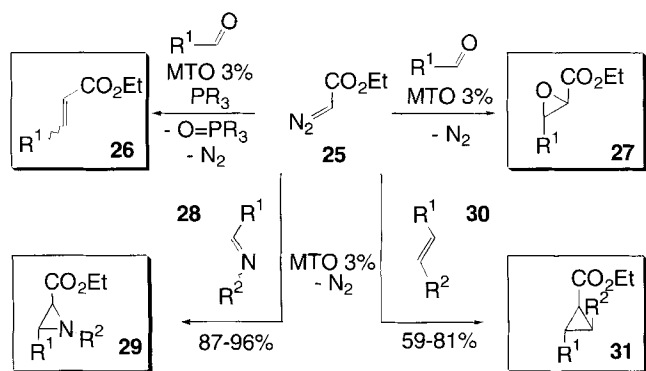


peroxide/urea system. Excess of oxidising agent gave the sterically crowded nitron (**24**). Quite obviously MTO-catalysed oxidations are a real addition to the chemical arsenal with high potential for organic synthesis.

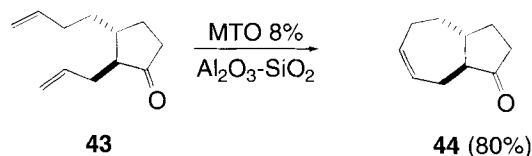
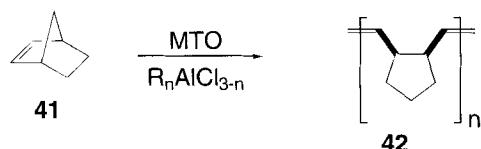
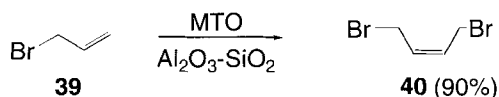
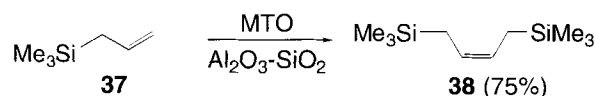
Olefination and cyclopropanation

Being more than just another oxidation catalyst, MTO catalyses the aldehyde-olefination by diazoalkanes. Equal amounts of aldehyde, diazoalkane (**25**), triphenyl- or tri-*n*-butylphosphine and catalytic amounts of MTO (3%) react to olefins (**26**, **32**, **34**), N₂ and phosphinoylides. Electron withdrawing substituents on the aldehyde lead to increased yield (*e.g.* **33**). The proposed mechanism starts by reduction of MTO to MeReO₂, which reacts with diazoacetate (**25**) to form a Me(O=)₂Re=CHCO₂Et carbene complex. Reaction with the aldehyde gives *via* metallaoxetane and subsequent cycloreversion the olefin (**26**) and MTO. This new aldehyde-olefination complements existing methodologies and is particularly useful for substrates prone to racemisation, because no base is required to form the carbenes or ylids of analogue reactions. Water-soluble phosphines give the opportunity to operate in two phase systems such as C₆H₆/H₂O. If the reactions are run without phosphines, *trans*-epoxides (**27**, **35**) will be isolated in good yields. Ketones undergo the same reaction, but are accompanied by 5–20% of the *Z*-isomer. The rates increase in the order: keton < aryl aldehyde < aliphatic aldehyde. A carbonyl replacement by imines (**28**) gives *trans*-configured aziridines

The oxidations by dioxiranes feature similar kinetics, chemo- and stereoselectivity. They offer an easy work up too, but have their limitations in instability, hence require fresh preparation. Peracids like *meta*-chloroperbenzoic acid demand more elaborate work-up and generally display lower chemo- and diastereoselectivity as seen in the epoxidation of geraniol to **17** and cholesterol to **18**. The more electron rich double bond is usually epoxidised first, resulting in good chemo-selectivity for polyunsaturated compounds. The reactions with MTO are generally faster than with any other d⁰ complex and tolerate a number of additional functionalities, such as alcohols, 3° amines and carbonyls, which are incompatible with some other oxidants. Sharpless epoxidations using oxophilic vanadium or titanium catalysts show opposite chemo-selectivity for geraniol (**16**). However, mercaptanes are oxidised to disulfides or sulfoxides. The sulfoxides are further oxidised to sulfones, yet at much slower rate. The sulfoxide formation as such may be a reversible oxygen transfer, hence care has to be taken of reactions involving dimethylsulfoxide [35]. On the other hand, pyridines and 3°-amines enhance both reaction rate and selectivity and are usually inert to oxidation. However, a high excess of hydrogen peroxide and 8% MTO converted pyridine into its *N*-oxide in quantitative yield [11b]. Secondary amines are oxidised *via* hydroxylamines to nitrones (**20**, **22**) in good to excellent yields by the MTO/hydrogen



(**29**, **36**) in excellent yields. Olefins react nicely under the same conditions to form cyclopropanes (**31**), but copper and rhodium catalysts are still superior and offer additional enantioselection. However, all of these methods are hampered by the availability and stability of diazoalkanes, limiting their scope to ethyl diazoacetate [EDA] and few other diazo compounds easy to obtain.



Olefin Metathesis

Metathesis of functionalised olefins was often limited by the organoaluminium additives required for catalyst activation. Particularly carbonyls and alcohols cause severe problems, this is due to undesired reactions or catalyst deactivation. These obstacles were overcome by Grubbs- and Schrock-catalysts and last but not least: MTO. The latter may be used either homogeneously or on solid support. The heterogeneous metathesis of acyclic olefins is carried out on MTO impregnated aluminium oxide at room temperature. The mild conditions disfavour side reactions like isomerisation, polymerisation or [2+2]dimerisation. The allyl derivatives (**37**, **39**) were converted into the 2-butenes (**38**, **40**) in good yields at high *cis*-diastereoselectivity. The MTO always equals and usually exceeds industrial rhenium catalysts. Suspensions of the MTO/Alox in dichloromethane or chlorobenzene allow metathesis of substrates with higher molecular weight. The ethenolysis of unsaturated fatty acid esters was carried out at an ethylene pressure of 7 kbar (7×10^8 Pa). Homogeneous Ring-Opening-Metathesis-Polymerisation (ROMP) of norbornene (**41**) in the presence of organoaluminium chlorides gave high molecular weight polymers (**42**).

The ability of MTO for Ring-Closing-Metathesis (RCM) was challenged by the synthesis of a hydroazulene (**44**), which derived from the diene (**43**), but in a rather slow reaction (7 days). Again the catalyst was supported on aluminium oxide. In spite of these encouraging results, the new generation of metathesis catalysts based on molybdenum and ruthenium is usually superior in yield and reaction rate. Paradoxically, the heterogeneous nature of the supported catalyst rules out an application in solid phase organic synthesis (SPOS), because the two reactants are trapped in different solid phases. Nevertheless, the MTO/Alox system offers simple catalyst recovery and such an ease of handling, that will set off some of its limitations.

In summary, this novel, fascinating catalyst with its high versatility and broad range of application belongs onto every organic laboratory shelf.

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