

Table 2. MTO-catalyzed ring-opening polymerization of norbornene (25°C, chlorobenzene, [Re]:[norbornene] = 1:500).

Cocatalyst	[Re]	[Al]	Polymer yield [%]	cis-Proportion of bonds [a] [%]	$\bar{M}_n$ [b] [g mol ⁻¹]	$\bar{M}_w$ [b] [g mol ⁻¹]	$\bar{M}_w/\bar{M}_n$
CH ₃ AlCl ₂	1	2	75	84			
	1	4	94	84	490 000	800 000	1.6
(CH ₃) ₂ AlCl	1	2	89	75	237 000	800 000	3.4
	1	4	94	47			
CH ₃ CH ₂ AlCl ₂	1	2	99	81	710 000	1 020 000	1.4
	1	4	79	62	142 000	510 000	3.6
(CH ₃ CH ₂) ₂ AlCl	1	1	97	83			
	1	2	90	79	160 000	370 000	2.3
	1	4	92	66	348 000	800 000	2.3
	1	8	92	58			

[a] Determination by ¹³C NMR. [b] Referred to polystyrene standard.

metals, molybdenum and tungsten, could also be optimized in this way. Moreover, catalytic properties are expected for the organic oxides of the neighboring element, osmium. Simple compounds such as O=Os(CH₃)₄ are known.^[13]

Experimental Procedure

MTO as heterogeneous catalyst: MTO (**1a**, 1.25 g, 5.0 mmol) was dissolved in 50 mL of CH₂Cl₂ and added to a well-stirred suspension of the carrier material [6], 130 g in 500 mL of CH₂Cl₂.

Metathesis of 1-hexene: CH₂Cl₂ (24.5 mL) was added to 1% of this contact suspension (3 wt % Re) in a 100 mL round-bottomed flask fitted with a nitrogen inlet and a reflux condenser. The mixture was treated with 1-hexene (5 mL, 40 mmol; Re:olefin = 1:800). The system was kept under slight positive pressure of dry nitrogen by means of a mercury check valve. (If the reaction was carried out under reflux to drive off the evolving ethylene, 93% of the initial olefin was converted after 30 min.) After fractional microdistillation of the reaction mixture 5-decene was isolated as *cis/trans* mixture. Yield: 2.0 g (77%). Comethathesis of methyl oleate and ethylene: CH₂Cl₂ (35 mL) and methyl oleate (1.7 mL, 5 mmol) were added to 1% of the contact suspension (Re: olefin = 1:100) in a 1000 mL laboratory glass autoclave and pressurized with 7 bar ethylene. After 2 h at room temperature 27% of the starting material had reacted (see Table 1).

Norbornene polymerization: To a solution of MTO (6.3 mg, 2.5 × 10⁻² mmol), chlorobenzene (3 mL), and CH₃AlCl₂ (100 μL of a 1 M solution in *n*-hexane) was added a solution of norbornene (1.2 g, 12.5 mmol) in 10 mL of chlorobenzene (Re:Al:olefin = 1:4:500). No starting material could be detected after 30 min. The reaction was stopped with 20 mL of methanol. A white polymer precipitated and was purified by dissolution in CHCl₃ and reprecipitation with CH₃OH. Yield: 1.1 g, 94%.

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Starting olefins of Table 2: a, 109-68-2; b, 592-41-6; c, 1119-51-3; d, 2695-47-8; e, 762-72-1; f, 18146-00-4; g, 557-31-3; h, 6140-80-3; i, 106-95-6; k, 25291-17-2; l, 80793-18-6; m, 27854-28-6; n, 68480-06-8; o, 2462-84-2. **1a**, 70197-13-6; Al₂O₃, 1344-28-1; SiO₂, 7631-86-9; CH₂=CH₂, 74-85-1; MeAlCl₂, 917-65-7; Me₂AlCl, 1184-58-3; EtAlCl₂, 563-43-9; Et₂AlCl, 96-10-6; NH₄ReO₄, 13598-65-7; SnMe₄, 594-21-4; (Z)-(BuCH₂)₂, 7433-78-5; (E)-(BuCH₂)₂, 7433-56-9; (MeCH₂)₂, 107-01-7; (EtCH₂)₂, 592-47-2; [Br(CH₂)₃CH₂]₂, 100960-98-3; [Br(CH₂)₄CH₂]₂, 137040-97-2; (TMSCH₂CH₂)₂, 3528-12-9; (TMSOCH₂CH₂)₂, 61549-43-7; (EtOCH₂CH₂)₂, 7250-85-3; (iPrOCH₂CH₂)₂, 88482-36-4; (BrCH₂CH₂)₂, 6974-12-5; (C₆F₁₃CH₂)₂, 56523-43-4; (C₆F₁₃CH₂CH₂)₂, 137091-62-4; [C₆F₁₃(CH₂)₂CH₂]₂, 137040-98-3; [EtCOO(CH₂)₈CH₂]₂, 137040-99-4; [Me(CH₂)₃CH₂]₂, 5557-31-3; [MeO₂C(CH₂)₃CH₂]₂, 13481-97-5; norbornene, 498-66-8; norbornene polymer, 25038-76-0; cyclopentane, 287-92-3.

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[6] Al₂O₃-SiO₂ containing 13 wt % Al₂O₃ (grain size > 15 μm) from Strem Chemicals Inc., Newburyport, MA, USA, was heated for 1 h at 550 °C in a stream of nitrogen and then doped with CH₃ReO₃. The catalyst must be handled in a dry atmosphere.
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Methyltrioxorhenium as Catalyst for Olefin Oxidation**

By Wolfgang A. Herrmann,* Richard W. Fischer, and Dieter W. Marz

Dedicated to Professor Karl Heinz Büchel on the occasion of his 60th birthday

The oxides of the neighboring elements of rhenium are active catalysts for olefin oxidation.^[1] They depend, however, on different mechanisms for their activity: With hydrogen peroxide, molybdenum and tungsten oxides form “inorganic peroxides” of type L_nM–OOH, which have proved to be efficient epoxidation agents. Osmium tetroxide reacts with olefins *cis*-stereoselectively—in stoichiometric and catalytic processes—to yield vicinal diols, which are formed via structurally defined osmate esters.^[1,2] However, no

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[**] Multiple Bonds between Main-Group Elements and Transition Metals, Part 100, second communication. (The first and third communications precede and follow this paper.) This work was supported by the Hoechst AG and the Fonds der Chemischen Industrie. Part 99: W. A. Herrmann, S. J. Eder, P. Kiprof, *J. Organomet. Chem.* 412 (1991) 407–414.

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organorhenium oxidation catalyst displays a high enough activity and selectivity under practicable conditions. Even in the current literature, doubts about rhenium and its compounds' potential for catalysis of olefin oxidations are expressed.^[1d, 3]

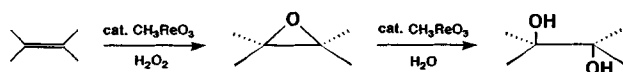
Although the simple rhenium oxides (such as Re_2O_7 , ReO_3 , and ReO_2), perrhenic acid, its inorganic esters (e.g. $(\text{CH}_3)_3\text{SnOReO}_3$), and the π complexes $[\text{C}_5\text{H}_5\text{ReO}_3]$ and $[\{\text{C}_5(\text{CH}_3)_5\}\text{ReO}_3]$ ^[4] activate neither oxygen nor peroxides, alkylrhenium oxides $\text{R}_n\text{Re}_2\text{O}_7$ in general,^[5] but especially the very stable, easily accessible methyltrioxorhenium (MTO, **1**), are highly active and selective catalysts for the oxidation of CC unsaturated compounds. In particular, **1** catalyzes the epoxidation of olefins with hydrogen peroxide. Both the alkene and the reaction temperature can be varied within a wide range (Table 1). The standard system $\text{MTO}/\text{H}_2\text{O}_2/$

Table 1. MTO-catalyzed epoxidation of olefins with H_2O_2 .

olefin	T [°C]	t [h]	product	yield [%] [a]
a) propene	-10	12	propenoxide 1,2-propanediol	50* [b] 50* [b]
b) 2-butene	-10	6	2,3-butanediol	100* [b]
c) <i>cis</i> -2-pentene	25	3	2,3-pentanediol <i>cis</i> -2,3-epoxypentane	10* 90*
d) 2,3-dimethyl-2-butene	25	1	2,3-dimethyl-2,3-butanediol	75
e) <i>trans</i> -4-octene	25	2	<i>trans</i> -4,5-epoxyoctane	95
f) cyclohexene	82	0.1	<i>trans</i> -1,2-cyclohexanediol	97*
	10	5	1,2-epoxycyclohexane	90
g) 4-vinylcyclohexene	15	2	1,2-epoxy-4-vinylcyclohexane 1,2-dihydroxy-4-vinylcyclohexane	50 40
h) 1-methylcyclohexene	25	2	1-methyl-1,2-cyclohexanediol	70
i) 1,4-cyclohexadiene	70	3	1,2,4,5-tetrahydroxycyclohexane	92
k) <i>cis,cis</i> -1,5-cyclooctadiene	0	1.5	5,6-epoxycyclooctene	80
l) cyclododecene	25	1	1,2-epoxycyclododecane	100*
m) β -pinene	5	0.1	β -pinene oxide β -pinane-1,2-diol	40* 50*
n) methyl oleate	25	24	methyl 9,10-dihydroxyoctadecanate	92
o) allyl alcohol	25	10	2,3-epoxy-1-propanol	90
p) crotylaldehyde	25	24	2,3-epoxybutaneal	60
q) 1,4-naphthoquinone	70	18	2,3-epoxy-1,4-naphthoquinone	64*
r) pentafluorophenylethene	25	24	1,2-epoxy(pentafluorophenyl)ethane	38

[a] Those yields marked with an asterisk were determined by GC/MS. All others refer to isolated products. [b] Yields relative to reacted olefin (reaction at ambient pressure).

$t\text{-C}_4\text{H}_9\text{OH}$ usually operates at room temperature with 0.1 to 1 mol % MTO with respect to the olefin. The yellow solution is stable for weeks below ca. 0°C and need thus not be freshly prepared.



Depending on the constitution of the epoxide, a ring opening that is also catalyzed by MTO can take place to form *trans*-configured 1,2-diols. In spite of the low pH of the catalyst solutions (pH $\approx$ 1–2) the activity of MTO can be traced not only to its Brønsted acidity but also to a metal effect.

Addition of an excess of amines such as 4,4'-dimethyl-2,2'-bipyridine, quinine, or cinchonine, suppresses the epoxide

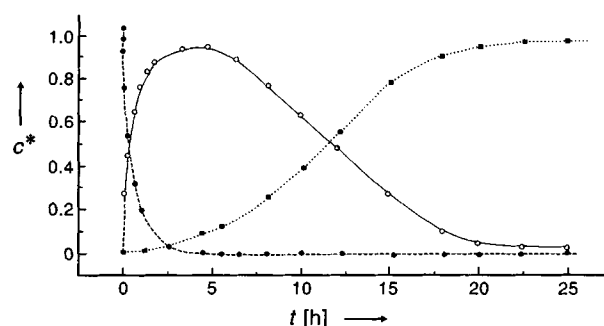
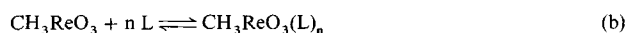


Fig. 1. Kinetics of the MTO-catalyzed cyclohexene oxidation. c^* = normalized concentration = $c(\text{starting material or product at } t = 0)/c(\text{cyclohexene at } t = 0)$. ● $c^*(\text{cyclohexene})$; ○ $c^*(1,2\text{-epoxycyclohexane})$; ■ $c^*(\text{cyclohexane-1,2-diol})$

ring opening even in 1,2-epoxycyclohexane, as a comparison of Figures 1 and 2 shows. Such amines lower the proton activity (pH $\approx$ 4) and form dissociation equilibria with the catalyst MTO^[4,5] [Eq. (b)].



Besides *tert*-butyl alcohols, solvents such as tetrahydrofuran, ethyl acetate, toluene, and water may be used. Temperature control is essential for reactive olefins because of the high catalyst activity.

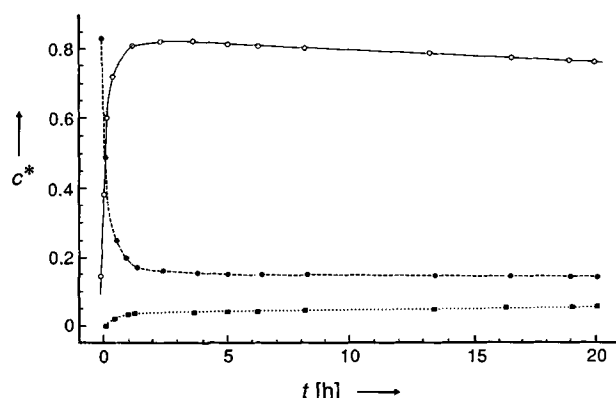


Fig. 2. Kinetics of the cyclohexene epoxidation with the MTO/coligand system. Labeling as in Fig. 1.

For storage a particularly stable form of MTO is easily prepared by warming a solution of MTO in distilled water, filtering the golden precipitate, washing with water, and drying in a vacuum. The solid is then pressed into 30–100 mg tablets. This procedure forms the first polymeric organometallic oxide:^[7] it has the approximate empirical formula $\{\text{CH}_3\text{ReO}_3\}_\infty$, is in contrast to sublimable MTO no longer volatile, is stable to air and moisture, and is insoluble in all noncoordinating solvents but soluble in hydrogen peroxide. Polymer-MTO is very simple to dose in tablet form.

An immobilization of MTO can be achieved by the addition of polymeric materials that contain the required basic center for rhenium attachment, in particular amine- and amide-nitrogen atoms. Typical examples are the commercially available polyvinylpyridines which are charged with 1–10 wt % MTO. This procedure also lowers the volatility substantially: the monomers cannot be removed from the carrier even when heated to 150°C under high vacuum. The advantage of this form of MTO lies in the easy recovery of the catalyst by filtration from the catalyst solution.

Although CH_3ReO_3 (MTO) and OsO_4 are isovalent molecules with similar structural and coordination chemistry—for instance, both yield stable adducts with amines like quinuclidine—they have different functions in the olefin/hydrogen peroxide system: in the first step OsO_4 forms osmate esters, which then undergo a stereoselective acid cleavage to afford vicinal *cis*-diols, whereas CH_3ReO_3 (unlike CH_3TcO_3 ^[8]) reacts *not* with the olefin, but with H_2O_2 to be transformed in a multistep reaction into a hydroperoxo complex, probably of constitution **C** (Scheme 1), which is an exceptionally selective epoxidizing agent.

CH_3ReO_3 (a 14e compound) has a more pronounced Lewis-acidity than OsO_4 (a 16e compound). One may assume that this is responsible for the different catalytic mechanisms. Although the catalytic species has not yet been fully characterized, the alkyl groups of MTO and its derivatives are clearly indispensable: on one hand, monitoring the olefin oxidation by NMR spectroscopy shows that the methyl group of the catalyst remains coordinated to MTO; on the other hand addition of methyl-cleaving reagents halts the activity immediately. In this way inactive perrhenate is formed on addition of base [Eq. (c)].



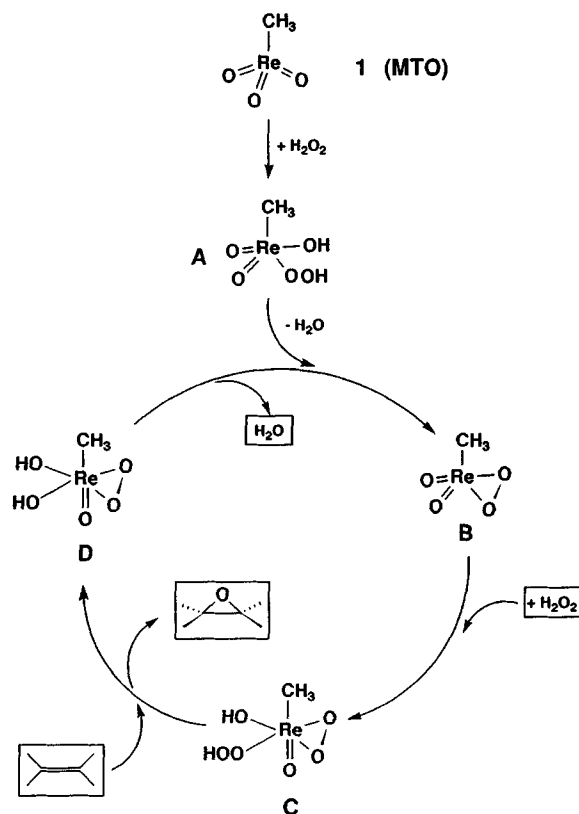
NMR and labeling experiments suggest the sequence of steps formulated in Scheme 1. There are *two* moles of H_2O_2 per mole of MTO required to form the active species **C** ($\delta_{\text{CH}_3} = 2.6$), which can be cleanly titrated against olefin. **C** can be extracted from MTO/perhydrol (a 30% H_2O_2 solution in water) into diethyl ether as a yellow complex and shows an IR band at 872 cm^{-1} typical for η^2 -peroxo complexes, but it has so far eluded isolation. After prolonged reaction times, methanol is formed as a deactivation product of MTO.

tert-Butyl hydroperoxide is neither formed in the oxidation solution described here, nor can it be activated by MTO for olefin oxidations. Even after a pretreatment of MTO with H_2O_2 , *t*- $\text{C}_4\text{H}_9\text{OOH}$ does not function as a primary oxidizing agent.

The $\text{MTO}/\text{H}_2\text{O}_2/t\text{-C}_4\text{H}_9\text{OH}$ system also oxidizes several alkynes: the major product from 3-hexyne is 4-hexen-3-one (*cis/trans*) in 55% yield; tolane yields 71% benzil. A catalytically accelerated Baeyer-Villiger oxidation can be performed with, for example, cyclobutanone.

The new class of oxidation catalysts is distinguished by a series of practical advantages: 1) High epoxide selectivity with the possibility of controlling the epoxide ring-opening kinetics through coligands, pH, and temperature; 2) high activity in a wide temperature range (-10 – $+100^\circ\text{C}$); 3) good stability of the oxidation-active system $\text{MTO}/\text{H}_2\text{O}_2/t\text{-C}_4\text{H}_9\text{OH}$ at low temperatures (storable for months at -30°C); 4) also active with electron-poor olefins (e.g. 2-bromo-2-butene) and simple gaseous olefins (e.g. propene, 2-butene); 5) use both as a homogeneous and a heterogeneous catalyst.

Furthermore, in no other epoxidation catalyst can the activity and selectivity be controlled as here by replacing the methyl groups with other alkyl groups. Important derivatives of the class of compounds have been described.^[10] In particular, electron-withdrawing substituents promise further applications in catalytic oxidation as a result of the enhanced Lewis acidity of their metal center. The derivatization of MTO through the oxo groups is also known.^[11] This also sets the new system aside from the "Milas reagents" (consisting of hydrogen peroxide and acidic metal oxides such as MoO_3 , V_2O_5 , and TiO_2), which have no constitutionally adjustable parameters.^[12a]



Scheme 1. Proposed mechanism for MTO-catalyzed epoxidation.

The oxidizing power of $\text{MTO}/\text{H}_2\text{O}_2$ is normally too weak for olefin cleavage, a reaction typical of ruthenium oxide catalysts;^[1b] stilbene and some styrene derivatives alone are cleaved oxidatively. Re_2O_7 is said to catalyze the oxidative cleavage of cycloolefins by H_2O_2 to ω,ω' -dicarboxylic acids, but only in boiling glacial acetic acid.^[12b]

Experimental Procedure

Oxidation solution: *tert*-Butyl alcohol (1 L) was kept at 30°C and mixed with 0.3 L of perhydrol. The solution was stirred with anhydrous MgSO_4 (200 g) for 3 h and then filtered.

Catalytic olefin oxidation: Catalyst **1** (10–50 mg, 0.04–0.2 mmol) was dissolved in oxidation solution (3–30 mL, 6–60 mmol of H_2O_2). The olefin to be oxidized (5–25 mmol) was added to this yellow catalyst solution, which was either cooled by ice, held at a constant temperature of 10 – 20°C , or allowed to react at ambient temperature. In the latter case the reaction mixture often reached boiling point (ca. 80°C). At the end of the reaction, which was indicated by a decolorization of the solution, any remaining H_2O_2 was decomposed with a catalytic amount of MnO_2 . The suspension was then filtered through a glass frit coated with celite, and the solvent removed under vacuum. The residue, a solid or a viscous mass, was either washed with or recrystallized from, common solvents (e.g. acetone, ethanol). Liquid products were distilled.

Oxidation of *cis*-1,4-dichloro-2-butene: MTO (0.3 g, 1.2 mmol) was dissolved in 100 mL oxidation solution (ca. 1.8 M in H_2O_2). *cis*-1,4-Dichloro-2-butene (15 mL, 0.14 mmol) was added dropwise to this yellow catalyst solution (molar ratio H_2O_2 :olefin:MTO = 150:120:1). The mixture was then stirred for 48 h at 25°C . After the addition of manganese dioxide (0.5 g) the gray suspension was filtered over a glass frit coated with celite. The solvent was removed from the colorless filtrate under vacuum (oil pump). The crude product (ca. 80% 1,4-dichloro-2,3-epoxybutane and starting material) was purified by Vigreux distillation. Yield 14.52 g (74%).

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MTO, 70197-13-6; propene, 115-07-1, 2-butene, 107-01-7; *cis*-2-pentene, 627-20-3; 2,3-dimethyl-2-butene, 563-79-1; *trans*-4-octene, 14850-23-8; cyclohexene, 110-83-8; 4-vinylcyclohexene, 100-40-3; 1-methylcyclohexene, 591-49-1; 1,4-cyclohexadiene, 628-41-1; *cis,cis*-1,5-cyclooctadiene, 1552-12-1; cyclododecene, 1501-82-2; β -pinene, 1330-16-1, methyl oleate, 112-62-9; allyl alcohol,

107-18-6; crotyl aldehyde, 4170-30-3; 1,4-naphthoquinone, 130-15-4; pentafluorophenylethene, 653-34-9; propene oxide, 75-56-9; 1,2-propanediol, 57-55-6; 2,3-butanediol, 513-85-9; 2,3-pentanediol, 42027-23-6; *cis*-2,3-epoxypentane, 3203-99-4; 2,3-dimethyl-2,3-butanediol, 76-09-5; *trans*-4,5-epoxyoctane, 1689-70-9; *trans*-1,2-cyclohexanediol, 1460-57-7; 1,2-epoxycyclohexane, 286-20-4; 1,2-epoxy-4-vinylcyclohexane, 106-86-5; 1,2-dihydroxy-4-vinylcyclohexane, 31646-64-7; 1-methyl-1,2-cyclohexanediol, 6296-84-0; 1,2,4,5-tetrahydroxycyclohexane, 35652-37-0; 4-cyclohexene-1,2-diol, 117919-55-8; 5,6-epoxycyclooctene, 637-90-1; 1,2-epoxycyclododecane, 286-99-7; β -pinene oxide, 6931-54-0; β -pinane-2,10-diol, 2005-76-7; methyl 9,10-dihydroxyoctadecanoate, 1115-01-1; 2,3-epoxy-1-propanol, 556-52-5; 2,3-epoxybutanal, 52788-68-8; 2,3-epoxy-1,4-naphthoquinone, 15448-58-5; 1,2-epoxy(pentafluorophenyl)ethane, 13561-85-8; *cis*-1,4-dichloro-2-butene, 1476-11-5; 1,4-dichloro-2,3-epoxybutane, 3583-47-9.

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Methyltrioxorhenium as Catalyst of a Novel Aldehyde Olefination**

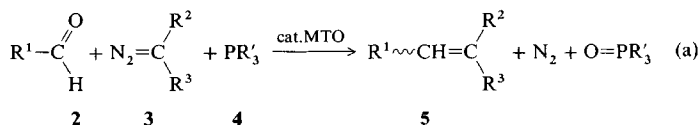
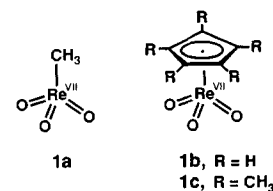
By Wolfgang A. Herrmann* and Mei Wang

Dedicated to Professor Karl Heinz Büchel
on the occasion of his 60th birthday

One of the most important syntheses for olefins is the Wittig reaction.^[1] Although restricted to the preparation of terminal double bonds, an organometallic variation that

uses the organotitanium Tebbe-Grubbs reagent is a particularly efficient process for open-chain and cyclic enol ethers.^[2] The driving force for this reaction is the high stability of the resulting TiO bond, which leads to drawbacks such as the necessity of stoichiometric quantities of the reagent. Here we describe the first aldehyde olefination catalyzed by a structurally defined organometallic compound.

Aldehyde **2** treated with diazoalkane **3** in the presence of an equimolar amount of a tertiary phosphane, preferably triphenyl- or tri-*n*-butylphosphane (**4a** or **4c**), affords the olefinic coupling product **5** according to Equation (a) if methyltrioxorhenium (MTO, **1a**)^[3a] is used as catalyst. Although the scope of the applications of this olefin synthesis has not been exhaustively studied, the advantages of easily accessible reagents, simple procedures, mild reaction conditions (room temperature), and good yields are apparent. In particular, diazoacetates and -malonates may be transformed with saturated and unsaturated aliphatic and aromatic aldehydes into the olefins **5** containing terminal carboxyl groups. Neither by a Wittig reaction nor with Tebbe-Grubbs reagents can this class of compound be synthesized. In contrast to MTO (**1a**), the π complexes **1b,c**^[3b] are not catalytically active.



- 2a**, R¹ = (CH₃)₂CH
2b, R¹ = C₆H₅CH=CH (*trans*)
2c, R¹ = (CH₃)₂C=CH(CH₂)₂CH(CH₃)CH₂
2d, R¹ = (CH₃)₂C=CH(CH₂)₂C(CH₃)=CH
2e, R¹ = C₆H₅
2f, R¹ = 4-BrC₆H₄
2g, R¹ = 4-NO₂C₆H₄
3a, R² = H, R³ = CO₂C₂H₅
3b, R² = CO₂CH₃, R³ = CO₂CH₃
4a, R' = (C₆H₅)₃
4b, R' = (*m*-C₆H₄SO₃⁻Na⁺)₃
4c, R' = (*n*-C₄H₉)₃

The reaction is generally carried out at room temperature by adding the diazoalkane dissolved in benzene or tetrahydrofuran dropwise to a solution of stoichiometric amounts of aldehyde and triphenylphosphane and a catalytic amount of MTO (1–10 mol %) in the same solvent.^[4] The reaction temperature (–20–+80 °C) has little effect on the product distribution. Minor products are formed in metal-catalyzed side reactions of the diazoalkane (formation of ketazines and olefins). Table 1 provides a preliminary summary of the scope of the new reaction. Existing double bonds or those being formed remain intact, because MTO does *not* catalyze cyclopropanation.^[5]

If the molybdenum complex [MoO₂{S₂CN(C₂H₅)₂}]₃ is used in place of MTO, the olefins derived from diazomalonnate according to Equation (a) are not obtained; instead stable phosphorus ylides are formed, which do not react with the aldehyde.^[6]

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