

Multiphase telomerisation of butadiene with acetic acid and acetic anhydride

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ABSTRACT

Two different routes to acetoxyoctadiene are presented. The first one uses the well-known telomerisation of butadiene with acetic acid operating in a multiphase semi-batch mode. The second reaction involves the cleavage of acetic anhydride, hydrogen transfer via ketene formation and thus a telomerisation as well.

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1. Introduction

Telomerisation reactions involve the dimerisation of a conjugated diene and the concomitant addition of a nucleophilic agent. Since 1966, when this homogeneously catalysed reaction was discovered by Smutny [1] and Takahashi [2], acetic acid has always been reported as a suitable nucleophile [3,4]. The telomerisation of 1,3-butadiene with acetic acid yields linear (1) and branched (2) acetoxyoctadiene (Fig. 1), which can be used as a starting material for the synthesis of numerous natural and flavouring materials [5,6]. As described for almost every telomerisation 1:1-adducts of diene and nucleophile, in this case acetoxybutenes (3,4), and a linear dimer of butadiene, 1,3,7-octatriene (5), are formed as by-products.

Especially Walker et al. [7] and Rose and Lepper [8] intensively investigated this reaction. All of their experiments were carried out discontinuously using condensed liquid butadiene. Palladium, which was provided as Pd(II)-complexes, was used as catalyst metal almost exclusively, triphenylphosphine (TPP) and -phosphite were mainly chosen as ligands.

Due to energetic reasons and in order to examine this telomerisation in terms of technical applications, it makes sense to provide the butadiene as gas under its vapour pressure and thus to carry out the telomerisation as a gas–liquid reaction. As Dehn [9] realised successfully for the nucleophiles methanol and water, a

semi-batch operation mode can be chosen using the set-up shown in Fig. 2. Before the run the reaction batch is provided in the reactor. To start the reaction the connection to the butadiene bottle is opened and the gas can flow in as much as consumed by the reaction, whereby the mass flow of butadiene into the reactor is measured and digitally recorded.

A further important requirement to a technical application is the recycling of the valuable palladium catalyst. Therefore the liquid–liquid biphasic technique may be used holding the catalyst and the product in different liquid phases (Fig. 3). This method is well investigated [10–12] and already industrially implemented by Kuraray Co. Ltd. for the telomerisation of butadiene with water [13]. Hence, in order to prove the technical potential of this reaction a polar catalytic system containing palladium bisacetylacetonate ($\text{Pd}(\text{acac})_2$) and the water-soluble ligand triphenylphosphine trisulfonate (TPPTS) was chosen.

2. Results

2.1. Multiphase telomerisation with acetic acid

Without additional solvent the telomerisation of butadiene with acetic acid does not take place in semi-batch runs, even the dimerisation of butadiene could not be observed. Variation of temperature, different concentrations of catalyst and ligand and the addition of bases like sodium acetate, which are used for activation in various telomerisations [14], did not activate the reaction in the semi-batch set up.

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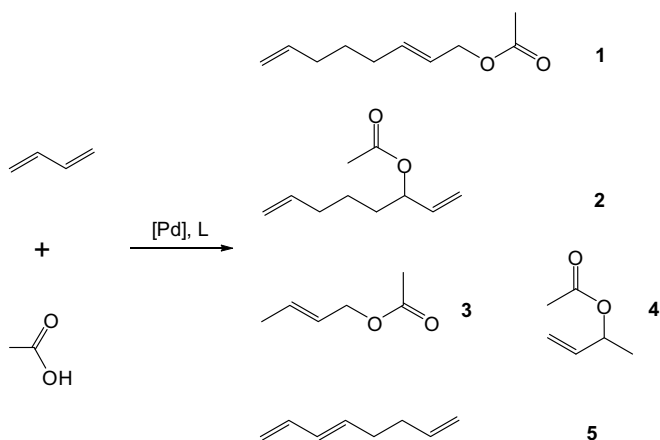


Fig. 1. Telomerisation of butadiene with acetic acid.

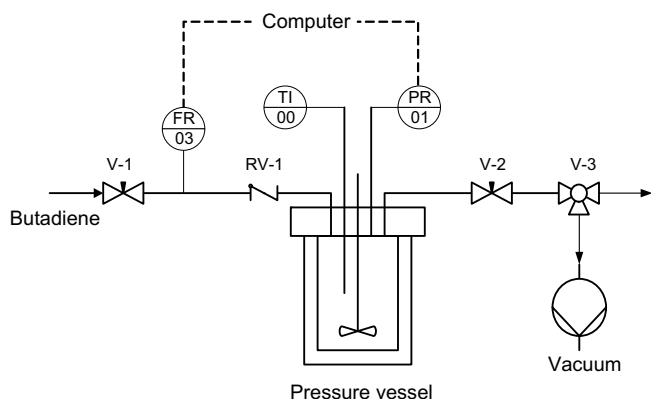


Fig. 2. Semi-batch set-up.

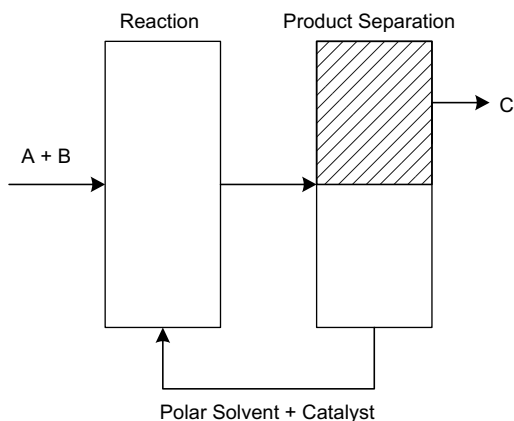


Fig. 3. Liquid-liquid biphasic technique.

When certain amounts of a solvent (here: 1,4-dioxane) are added to the reaction batch, telomerisation sets in obtaining greater yields of telomer at lower concentrations of acetic acid (Table 1). It also can be noticed that the dimerisation is repressed due to dilution.

These results indicate that under the given conditions the catalyst is blocked by coordinating acetic acid molecules thus preventing that the butadiene can reach the palladium coordination sites sufficiently. When the ratio of butadiene to acetic acid is increased, both by the reduced amount of acetic acid and by the greater solubility of butadiene in the liquid phase due to greater amounts of dioxane, telomerisation reaction takes place.

Table 1

Semi-batch telomerisation with acetic acid in dioxane (w = mass fraction, X = conversion of butadiene, S = selectivity, $\text{Pd}(\text{acac})_2$, TPP, 5 h, 70 °C)

w (HOAc) (-)	X (%)	S (Telomer) (%)	S (1:1-Adducts) (%)	S (Dimer) (%)
0.2	38	85	11	3
0.5	19	79	13	8
0.8	8	43	28	30

Furthermore, acetic acid was found in batch and semi-batch experiments not suitable for the liquid-liquid biphasic technique and thus for a gas-liquid-liquid reaction mode. If the reaction batch contains water or a different polar solvent as propylene carbonate, dimethyl sulfoxide or sulfolane, telomerisation reaction does not take place, even with additional bases like sodium acetate or triethylamine.

2.2. Telomerisation with acetic anhydride

We observed that the acetoxyoctadienes were also formed when acetic anhydride was used as reactant instead of acetic acid. This is astounding since obviously the anhydride is not a typical nucleophile. However, the general question comes up why the telomerisation with an anhydride can actually take place. Telomerisation is described generally by the mechanism of Jolly [15,16]. In case of acetic acid the mechanism of Keim [17,18] may also be consulted considering the formation of acetate-bridged bis-palladium complexes. However, both mechanisms consistently claim that for telomerisation the nucleophilic agent (telogen) must have an active acidic hydrogen atom which is contained in acetic acid but not in acetic anhydride. Hence, telomerisation with anhydrides is not described in literature up to now.

2.2.1. Discussion of mechanism

An obvious explanation for the reaction observed is that solely acetic acid, which is always accompanied with acetic anhydride in a small amount due to production reasons, undergoes telomerisation and that acetic anhydride generates fresh acetic acid by hydrolysis with dissolved water. However, it could be shown by analysis via GC-FID that these amounts of acetic acid are by far too little to form the amount of telomer obtained in the reaction. In addition, hydrolysis is reported to be very slow in pure anhydride medium, as investigated by Orton and Jones [19]. Own measurements with Karl-Fischer-Titration showed that in the course of an experiment always less than 200 ppm of water (for 60 ml: 0,7 mmol) are consumed.

Two sets of experiments clarify the role of the acetic acid which is present in the reaction batch:

- If acetic acid is added to a reaction batch containing only acetic anhydride and the catalytic system, the telomerisation does not take place. Hence, in this case acetic anhydride does not act as a solvent which would prevent the limitation of the telomerisation with acetic acid by the concentration of butadiene (as in Table 1).
- If small amounts of water are provided along with the anhydride, telomerisation still does not occur. This indicates that not just the fresh acetic acid, which is formed by hydrolysis of the anhydride, undergoes telomerisation.

Hence, it may be assumed that during telomerisation of butadiene with acetic anhydride a cleavage of the anhydride takes place. Since the thermal cleavage of acetic anhydride yielding ketene and acetic acid exclusively occurs at temperatures above 400 °C [20], that means way above the usual reaction temperature of 70 °C, it

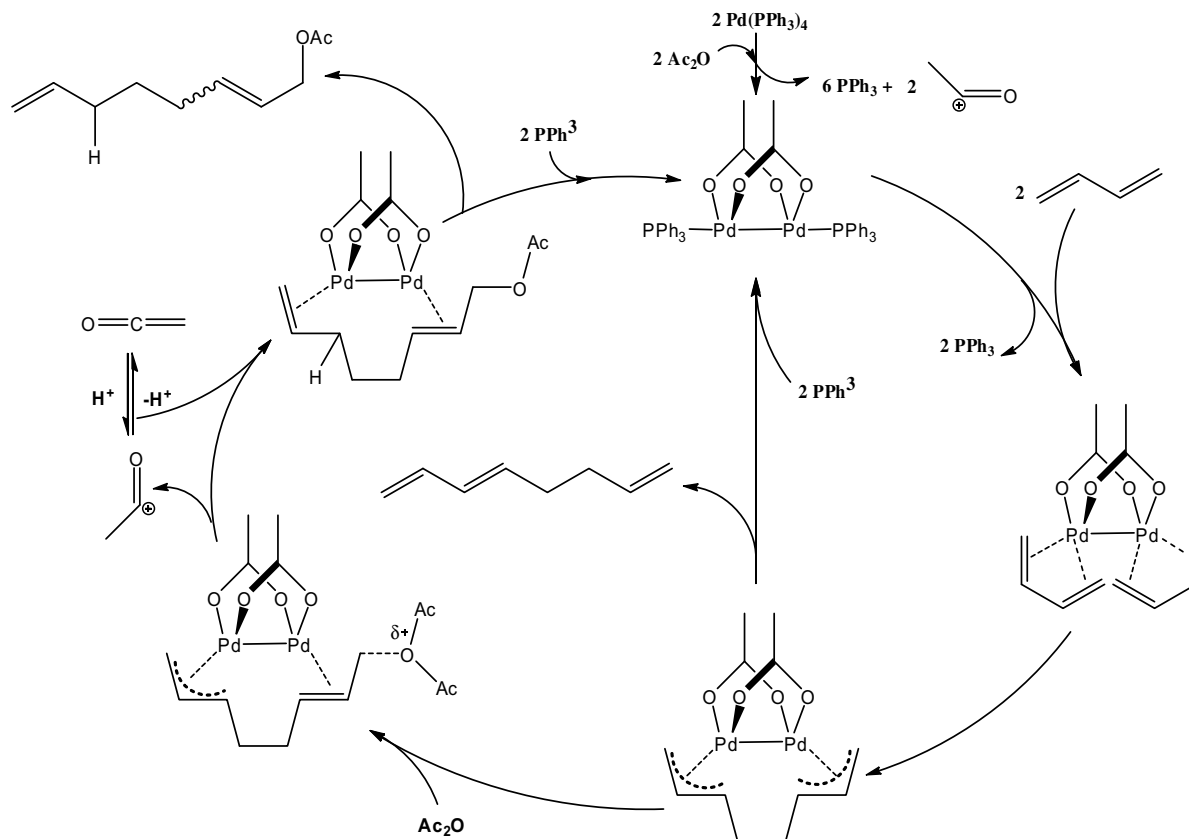


Fig. 4. Extended Keim-mechanism for the telomerisation of butadiene with acetic anhydride.

can also be supposed that the formation of acetate-bridged bis-palladium species, as described in the mechanism of Keim, causes this cleavage (Fig. 4). An acetyl cation, whose properties are well described by Tidwell [21], is split off, deprotonates forming a ketene and thus delivers the necessary hydrogen to telomerisation, whereas ketene reacts with diverse reactants itself. At first it undergoes reactions with acetic acid yielding acetic anhydride and at lower level with dissolved water forming acetic acid.

2.2.2. Batch experiments

A typical batch experiment with butadiene provided liquidly obtains 51% conversion of butadiene and the selectivities that are shown in Table 2. Apart from the telomer large quantities of octatriene and very little of the 1:1-adducts are formed. In addition, mass spectroscopic methods identify small amounts of further (partly unidentified) by-products, which mainly are adducts of ketene with the dimer and the telomer, respectively.

Various reactions of the very reactive ketene are known for a long time, e.g. the dimerisation or the cycloaddition to conjugated dienes [22,23]. Vinyl cyclobutanone, which is formed by the addition of ketene and butadiene, could not be detected in this case.

Table 2
Selectivity, batch mode 20 h, 80 °C

Telomer	64
Dimer	32
1:1-Adduct	<1
1:1-Adduct Ketene:Dimer	<1
2:1-Adduct Ketene:Dimer	1
3:1-Adduct Ketene:Dimer	<1
1:1-Adduct Ketene:Telomer	1

However, Vogel et al. [24], who discovered this reaction, worked with much higher concentration of ketene and obtained only low yields of the cycloadducts. Diketene was also not observed after the reaction, possibly because of diverse fast consecutive reactions.

In the reaction solution dissolved ketene could be detected showing the MS-spectrum presented by Tidwell [21]. Besides these rather small amounts, the headspace was assumed to contain more of unreacted ketene. In order to confirm this, the headspace was bubbled through diethylamine yielding significant amounts of diethylacetamide, which again argues for the existence of ketene intermediates. In an analogue test with ethanol the formation of ethyl acetate, which is the product of ketene alcoholysis, could be observed.

When d_6 -acetic anhydride is used, the significant mass peaks of the telomer are shifted by 4, which again indicates the cleavage of acetic anhydride and the ketene forming mechanism.

2.2.3. Semi-batch experiments

The telomerisation with acetic anhydride was also investigated under semi-batch conditions. For all runs the flow of butadiene into the reactor showed the same behaviour, which is presented in Fig. 5 (left axis).

In the beginning of the reaction butadiene fills the headspace and then saturates the liquid phase due to high agitation rates (1200 rpm). The actual reaction is observed to start after app. 80 min. The conversion (right axis) and thus the flow of butadiene increase significantly. This autocatalytic behaviour may be explained by the deprotonation equilibrium of the acetyl cation. Since one cation forms two reacting species, the reaction rate accelerates. The rise of the reaction rate stops after app. 110 min. From this point on an increasing darkening of the sample liquid

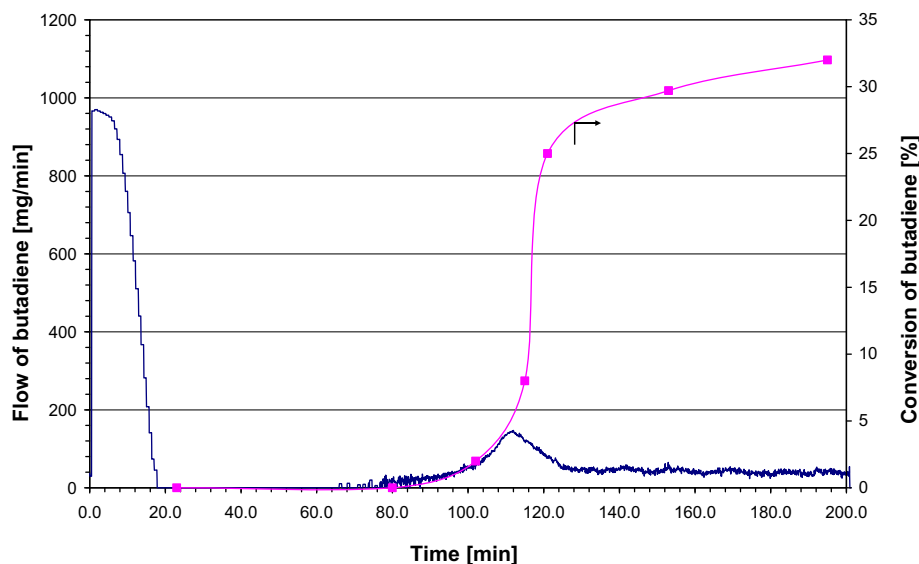


Fig. 5. Flow and conversion of butadiene vs. time, 70 °C.

is noticed and triphenylphosphine is found oxidised for the most part (with increasing proportion). It is still to investigate why this oxidation, which in batch runs is almost complete by the end of the reaction, occurs. Since all operations have been done under strict exclusion of oxygen, it is likely that an attack of bound oxygen takes place. As the triphenylphosphine does not get oxidised without the addition of butadiene and with all the other reaction parameters kept the same, it may be assumed that the reaction is responsible for the oxidation of the ligand and that this change in the catalytic system causes the fall of the reaction. Mass spectroscopic analyses show small amounts of various derivatives of triphenylphosphine fragments like acetophenone.

Nevertheless, the reaction rate remains steadily on a lower level, whereas the amount of dimer increases as shown in Fig. 6. This increase and thus the great amount of dimer in batch experiments may be explained by the insufficient accessibility of hydrogen, which is essential to telomerisation. The amount of acetic acid and water, which is already very small before the beginning of

the reaction, decreases continuously during the reaction. After these hydrogen resources have run dry, the telomer is no longer formed, which only leaves the route to the dimer in the mechanism (Fig. 4).

The by-products, which were identified in batch experiments, are also observed, but occur in minor amounts.

2.2.4. Further influencing factors

When bases as triethylamine are added, the reaction of butadiene and acetic anhydride does not yield the telomer, but only the dimer (Table 3). Since these bases accelerate telomerisations which involve nucleophiles, it is therefore likely again that a regular telomerisation does not take place using this reaction system. It may be assumed that the amine prevents the essential transfer of hydrogen thus suppressing telomerisation but not dimerisation.

By diluting the reaction batch with an additional solvent like dioxane a lower conversion of butadiene is obtained. Due to a lower availability of hydrogen the amount of dimer increases.

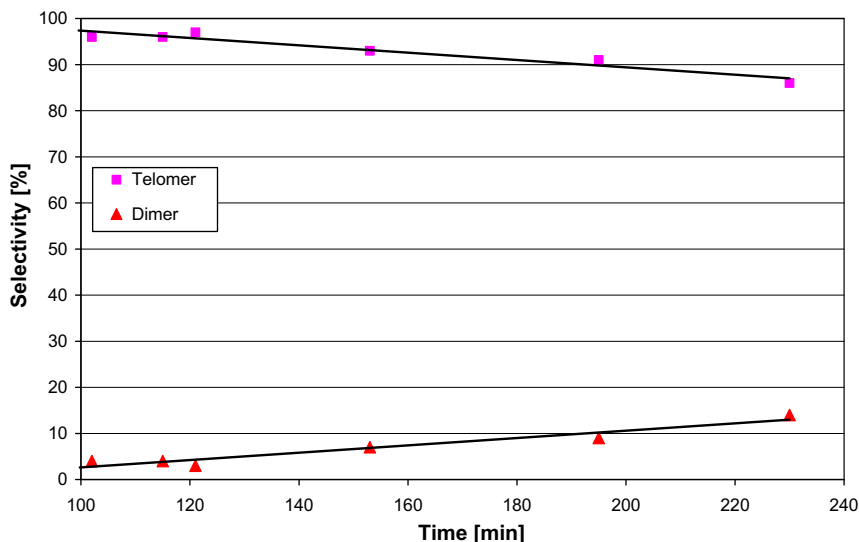


Fig. 6. Selectivity towards telomer and dimer vs. time.

Table 3

Semi-batch runs: [1] standard run; [2] addition of 2 g triethylamine; [3] 50 wt% 1,4-dioxane (X = conversion of butadiene, S = selectivity)

Run	X (%)	S (Telomer) (%)	S (Dimer) (%)
[1] Standard	32	91	9
[2] Addition of triethylamine	8	0	100
[3] Additional solvent	11	81	16

2.3. Telomerisation of butadiene with ethyl acetate

Further on, it was investigated whether there are more reactants being able to build acetate-bridged bispalladium complexes as strong as necessary to cleave the reactants. It was found that acetoxyoctadiene is also formed in the reaction of butadiene and ethyl acetate. Admittedly this reaction system is not very active obtaining only 2% yield of telomer. Hence, it is assumed that an ethyl cation splits off the ethyl acetate in an analogous manner as described in the mechanism for acetic anhydride (Fig. 4), but that this cation is not able to deliver the hydrogen, which is necessary for telomerisation, as much as the acetyl cation.

3. Conclusions

Acetic acid was found not suitable for the telomerisation of butadiene in terms of a multiphase application of the liquid–liquid biphasic technique. In semi-batch gas–liquid reactions acetic acid does not show activity unless a solvent as dioxane is added. At a lower initial concentration of acetic acid higher yields of telomer are obtained, which indicates a blocking of the catalyst by the acid under the given conditions.

The ester acetoxyoctadiene, the product of the telomerisation of butadiene with acetic acid, is also formed by the palladium-catalysed reaction of butadiene and acetic anhydride. It could be shown that this reaction is not just a hidden telomerisation with acetic acid and that acetic anhydride is actually converted. Therefore it may be assumed that due to the formation of acetate-bridged bispalladium complexes a cleavage of the acetic anhydride takes place. An acetyl cation is split off, deprotonates yielding ketene and thus delivers the necessary hydrogen for telomerisation. Ketene undergoes various side reactions itself. This proposed mechanism based on the mechanism of Keim was also verified by experiments with d_6 -acetic anhydride.

Traces of acetoxyoctadiene are also formed by the reaction of butadiene and ethyl acetate. This again indicates the formation and stability of the bispalladium complexes, which are presumably able to cleave ethyl acetate in low yields.

Summing up, it could surprisingly be proven that telomerisation also takes place without a reactant containing active hydrogen.

4. Experimental

4.1. Chemicals

Triphenylphosphine was purchased from Acros and used without further purification. Palladium bisacetylacetonate was donated

Table 4

Starting compounds and typical reaction conditions

Compound	(mmol)	(g)	Reaction conditions
Acetic anhydride	637	65	Temperature 70 °C
Pd(acac) ₂	0.33	0.1	Pressure <2.3 bar
TPP	1.91	0.5	Agitation rate 1200 rpm
			Reaction time 5 h
			Volume of liquid 60 ml

by Umicore AG & Co. KG. Triphenylphosphine trisulfonate was acquired from OXEA GmbH. Acetic acid (purity 99.8%), acetic anhydride (purity 99.5%) and 1,4-dioxane (purity 99+%) were also purchased from Acros. 1,3-Butadiene (purity 99.5%) was acquired from Air Liquide.

4.2. Instrumental

All batch and semi-batch reactions were carried out in 300 ml pressure vessels, model 4561 (Parr Instruments). The reactor consists of a steel bomb and a steel cover, which includes the armatures for filling and regulation and a rupture disc.

Before the semi-batch runs the complete set-up was evacuated and flushed with argon several times. Then the reaction batch was sucked into the reactor. When reaction temperature was reached, the connection to the butadiene bottle was opened. The mass flow of butadiene thereby was measured using a thermal mass flow meter by Bronkhorst High-Tech (model EL FLOW F-201C). The system pressure was detected by an electrical pressure meter by Bronkhorst High-Tech (model EL PRESS P-502C). The heating of the reactor took place using an electrical heating jacket. The temperature was measured by a thermocouple, which is attached to a PID automatic controller (Parr type 4842). Stirring was performed using a standard turbine type impeller.

Batch preparations were carried out under flow of Argon thus preventing the oxidation of the substances.

In a typical reaction using the ligand triphenylphosphine (TPP), the following quantities of starting compounds and reaction conditions were used (Table 4).

All results were reproduced several times.

The product sample was analysed by GC/FID (HP 6890) and GC/MS on a HP-5 phenylmethylpolysiloxan column (length 30 m, diameter 250 μ m, layer thickness 0.25 μ m) with *n*-heptane as internal standard for the acetoxyoctadiene.

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