ARTICLE

Selective dihydroxylation of methyl oleate to methyl-9,10-dihydroxystearate in the presence of a recyclable tungsten based catalyst and hydrogen peroxide

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The dihydroxylation of fatty methyl esters is of prime importance for the synthesis of surfactants and lubricants. The conversion of methyl oleate (MO) to 98% yield of methyl-9,10-dihydroxystearate (MDHS) was performed in the presence of H_2O_2 and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst in absence of a phase transfer agent. The study of the effect of hydrogen peroxide concentration revealed that significant catalytic activity was only achieved for an optimal amount of H_2O_2 . A mechanism for this reaction was proposed where hydrogen peroxide reacts with $\text{H}_3\text{PW}_{12}\text{O}_{40}$ to produce peroxo-phosphotungstate anions, which directly dihydroxylate MO. The recyclability of the catalyst was also studied. To this aim, a recyclable form of the heteropolyacid was synthesized using Cs cations ($\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$). This catalyst was recycled up to three cycles without significant loss in catalytic performances.

Introduction

Fatty acid methyl esters (FAME) received a lot of attention as a source of value-added chemicals owing to their low price and the fact that they can be converted into several multifunctionalized molecules through a relatively small number of synthetic transformations. Thus, FAME is an important starting material in a number of reported reactions, in particular, the production of biodiesel through esterification reactions,^{1–8} and the oxidative functionalization of FAMEs to produce epoxides or acids used in a broad range of industrial applications such as lubricants, plasticizers, hydraulic fluids, pharmaceuticals for skin diseases and cosmetic auxiliaries.^{7,9} Presently, many reactions can be performed from C=C transformation of this class of molecules, but the most investigated are epoxidation and C–C cleavage reactions.^{10–12} One interesting reaction is the dihydroxylation of FAME or fatty acids to produce the corresponding diols which are used for the manufacture of surfactants and lubricants. This reaction can be performed through two mechanism pathways (Scheme 1).

Scheme 1. Reaction pathways for the dihydroxylation of methyl oleate.

The first pathway (A) is the formation of diols *via* epoxidation of the double bond and hydrolytic cleavage by water. In this pathway, it is of importance to mention that this reaction sequence was often used without detection or isolation of the intermediately formed epoxides. Catalysts used for this reaction are essentially based on W or Mo.^{13–18} One can mention that in many studied reactions, diols are often observed as intermediates in the full cleavage reaction, and are considered as intermediates or by-products resulting from the epoxidation of the double bond, but they are not the targeted products.¹¹ The second pathway (B) is the direct dihydroxylation of the double bond. The direct dihydroxylation reaction (pathway B) of unsaturated fatty acids or esters was reported with Os or Ru based catalysts and various co-oxidants to reoxidize the reduced metal species, *e.g.* hydrogen peroxide, *tert*-butyl hydroperoxide, *N*-methylmorpholin-*N*-oxide or potassium hexacyanoferrate (III).¹⁹ The direct dihydroxylation was also performed using stoichiometric amount of permanganate. New Os-containing catalysts were also investigated in the presence of molecular oxygen²⁰ leading to diols used for the manufacture of surfactants. For example, 85% of methyl-9,10-dihydroxystearate (MDHS) were obtained from methyl oleate (MO) using a mixture of THF and water, with a THF/ H_2O volume ratio of 3:1 as solvent, in the presence of OsO_4 and 4-methylmorpholine *N*-oxide.²¹ MDHS was used in that work as an intermediate for the synthesis of lubricity improver which contains at least one 1,2-dimethoxyester. All methods mentioned above to produce diols present several drawbacks, including the use of organic solvents without recovery, the reliance on more than one step to produce the desired product and sometimes the need for expensive and toxic oxidants. Among the usual oxidants used, H_2O_2 is considered as an attractive candidate since it is produced annually in 2.2×10^6 tons worldwide, almost exclusively (> 95%) by means of the

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alkylanthraquinone autoxidation process, and only leads to water molecules as by-products when it is used in an oxidation reaction.²² The H₂O₂-mediated direct dihydroxylation of unsaturated fatty acids or esters was studied in the presence of a Fe-tetra amido macrocyclic complex²³ or a resin-supported sulfonic acid under metal-free conditions without any organic solvent.²⁴ In this study, they used Nafion SAC-13 at 90°C in the presence of 30% of H₂O at 70°C for 20h affording 80% yield of the diols from oleic acid. Piazza *et al.* showed that alumina-catalyzed hydrolysis of fatty epoxides is an efficient way to synthesize polyhydroxy materials.²⁵ Cecchini *et al.* reported the oxidation of FAMES (methyl oleate, methyl linoleate and methyl linolenate) using oxovanadium complexes in the presence of CHCl₃ as solvent, where the best yield in MDHS was 87% along with 13% of epoxide after 6 h reaction at 50 °C.²⁶ H₂O₂ is widely used as oxidant in biomass conversion to chemicals and some examples reported the combination of H₂O₂ and tungstic acid for fatty acids conversion to dicarboxylic acids, azelaic acid, etc.²⁷ For example, a high conversion of 90% and 80% selectivity in desired diol during dihydroxylation reaction was observed in the presence of this system. One can mention that a concentrated solution of H₂O₂ (> 60%) is required and should be added continuously to convert fatty acids.^{28,29} The use of an excess of H₂O₂ is problematic on large scales due to safety considerations.³⁰ In the case of low concentrated solution of H₂O₂, the sheer volume of the aqueous reagents required can be detrimental to the reaction and phase transfer agent are required.

The synthesis of diols from FAME require the control the selectivity and a concentrated solution of H₂O₂. In order to use a low concentrated solution of H₂O₂, mass transfer agent are often used in order to reach a yield to diols over 70%. The catalysts used for this reaction are often homogeneous ones and not recyclable. Herein, we wish to demonstrate that methyl-9,10-dihydroxystearate (MDHS) can be produced from methyl oleate (MO) using a one step process without the addition of an organic solvent or a mass transfer agent in the presence of an aqueous solution of H₂O₂ (30%). Peroxo-phosphotungstate (POW) based catalyst can be used to perform epoxidation reaction in a biphasic media containing an organic solvent as demonstrated by the work of Venturello and D'Aloisio.^{31,32} Previously, we have shown that an amphiphilic dipyridinium peroxo-phosphotungstate ion pair was selective and recyclable catalyst for the triphasic epoxidation of fatty acids and esters with hydrogen peroxide.³³ Based on these results and on the state of the art, tungsten based catalyst (H₃PW₁₂O₄₀) were chosen to synthesize MDHS. This catalyst was studied without the use of a phase transfer agent or organic solvent. We also developed a recyclable version of this catalyst (and Cs_{2.3}H_{0.7}PW₁₂O₄₀) relying on a cation exchange with Cs²⁺.

Experimental

Materials and methods

Hydrogen peroxide (30 wt% aqueous H₂O₂) purchased from Acros-Organics was used as primary oxidant. Methyl Oleate (MO), from Alfa Aesar, was purchased with a purity of 96% and phosphotungstic acid H₃PW₁₂O₄₀, from Sigma-Aldrich, was used as an acid catalyst. 9,10-Epoxy methyl stearate (epoxide) was purchased with 99% purity from Santa Cruz factory from Toronto and was used as a calibration standard to quantify the yield of the produced epoxide. In order to quantify MDHS (methyl-9,10-dihydroxystearate) was synthesized with a 80% purity from the oxidation of methyl oleate for quantification purposes. The purity of MDHS was verified by NMR and LCMS analysis and the MDHS was then used as a calibration standard. The carbon mass balance was checked by ¹H NMR and mass spectrometry analysis.

Catalytic tests

All catalytic experiments were carried out in a 50 mL glass flask fitted with reflux, starting from 5 mmol of the substrate (methyl oleate) in the presence of 5 wt% of catalyst and the desired amount of aqueous H₂O₂ (30%) (from 1.1 eq. (0.63g) to 1.5 eq. (0.86g)). The reaction mixture was stirred (1400 rpm) at the defined temperature (from 50 to 80°C). At the end of the reaction, the reaction media was cooled down rapidly and the organic phase was extracted using ethyl acetate (40 mL) and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the sample was diluted using 1 mL of pyridine and silylated by adding hexamethyldisilazane (1 mL) and chlorotrimethylsilyl (1 mL). Sorbitol (2 mg), used as external standard, was added to the sample before analysis by GC-FID. Each result corresponds to one experiment, and no sample was taken.

GC-FID analyses

Gas chromatography analyses (GC-FID) were performed using an Agilent Technologies 456 series instrument equipped with a flame ionization detector, using a column of 30 m×0.25mm×0.5 µm film thickness composed with phenyl (5%) dimethyl siloxane (95%).

The conversion values of methyl oleate was calculated as shown below:

$$\text{Conversion (\%)} = \frac{A_{MO}^i/A_{sorbitol} - A_{MO}^t/A_{sorbitol}}{A_{MO}^i/A_{sorbitol}} \times 100$$

Where A_{MO}^i and A_{MO}^t represent the values of the area of methyl oleate chromatographic peaks respectively at the initial time (time zero) and time of control. $A_{sorbitol}$ is the area of the external standard.

The yields of products (MDHS and epoxide) at time of control t were calculated as shown below:

$$\text{Yield (\%)} = \frac{\text{mol of product formed}}{\text{initial mol of methyl oleate}} \times 100$$

Where A_p^i and A_p^t represent the values of the area of the product (MDHS or epoxide) chromatographic peaks respectively at the initial time (time zero) and time of control. The margin error for yields and conversions is around 3% for all the results.

Results and discussion

In a first set of experiments, 5 wt% of phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) was added to 5 mmol of methyl oleate (MO) in the presence of 1.1 eq. of H_2O_2 at 80 °C (Figure 1). After 2 min of reaction, 15% of MO was converted and MDHS was produced with 14% yield. Upon prolonged reaction time, conversion of MO reached a maximum of 85% after 2 h of reaction with yields of 84% and 1% in MDHS and epoxide, respectively. Interestingly, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the presence of H_2O_2 featured an impressive selectivity to MDHS of over 99% throughout the reaction duration.

Figure 1. Oxidation of methyl oleate (5 mmol) to MDHS and epoxide in the presence of 5 wt% of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and 1.1 eq. of H_2O_2 at 80 °C.

Reaction conditions were then explored with the aim to decrease the amount of both catalyst and H_2O_2 used in the oxidation of MO. In all experiments described hereafter, the selectivity to MDHS remained higher than 98%, and thus, for simplicity, results were solely expressed in terms of MO conversions.

First, the acid catalyst loading was studied at 80 °C in the presence of 1.1 eq. of H_2O_2 (Figure 2).

Figure 2. Effect of catalyst amount on the conversion of methyl oleate using 1.1 eq. of H_2O_2 , 5 mmol of MO at 80 °C (the yield in epoxide in all these experiments was less than 2%).

The decrease in catalyst amount from 10 wt% to 5 wt% led to a slight change at the beginning of the reaction (up to 30 min) and after 30 min of reaction, similar trend was observed and both catalyst loadings enabled 85% conversions after 2 h of reaction (Figure 2). The initial rate of the reaction increased from 165 h^{-1} to 842 h^{-1} from 10 to 5 wt% loadings. A further decrease of the amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ from 5 wt% to 2 wt%, led to a smaller initial reaction rate from 842 h^{-1} to 672 h^{-1} but a complete conversion of MO was observed after 2 h of reaction with a catalyst amount of 2wt%. For 1 wt% of catalyst loading, the reaction slowed significantly, with conversions systematically lower at all-time points than all of the 3 other studied loadings for a reaction time lower than 100 min. Above 100 h the MO conversion is 90% against 85% for 5 wt% and 10 wt%. The initial rate of the reaction was thus very low (95 h^{-1}) in the presence of 1 wt% of catalyst and the conversion reached 90% after 2 h of reaction. These results suggest that an optimal loading was obtained at 2wt%, which can be rationalized by the fact that an excess of catalyst may lead an excessively fast decomposition of H_2O_2 , while too low loadings fail to sustain the reaction as it is reported in the literature.³⁴ At this loading, we observed the highest MO conversion (100%) as well as the highest yield in MDHS (99%), at 80 °C using 1.1 eq. of H_2O_2 . It seems that it is necessary to control the ratio catalyst/ H_2O_2 to obtain good MDHS yields from MO. In order to confirm this observation, the effect of H_2O_2 content on the conversion of MO was then studied (Figure 3). Variations in the amounts of H_2O_2 had drastic effects on the conversion. When decreased from 1.1 eq. to 0.5 eq. (molar), the conversion of MO decreased from 98% to 45%, while the selectivity in MDHS remained high at 99% after 90 min of reaction. Increasing oxidant content to 1.5 eq. led surprisingly to only 1% conversion of MO. The H_2O_2 quantity was varied by altering the volume of its 30 wt% aqueous solution, thus increased H_2O_2 content resulted in larger volumes of the aqueous phase. The existence of an optimum H_2O_2 content at 1.1 eq. may be explained by the fact that at lower amounts, the conversion is limited by the actual quantity of reagents available.

Figure 3. Effect of the hydrogen peroxide content on the conversion of methyl oleate using 5 mmol of MO and 2 wt% of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ at 80 °C (the yield of epoxide in all these experiments was less than 2%).

If H_2O_2 was added dropwise (1.1 eq.) with a flow of $0.05 \text{ mL}\cdot\text{min}^{-1}$ and that the reaction took place for 1 h after the addition of H_2O_2 , 78% of MO was converted to 77% of MDHS. If the addition flow of H_2O_2 was increased from $0.05 \text{ mL}\cdot\text{min}^{-1}$ to $0.07 \text{ mL}\cdot\text{min}^{-1}$ and the reaction was pursued for 1 h the conversion of MO reached 96% and 95% of MDHS was produced. These results showed that in this case by playing on the addition rate of H_2O_2 similar results are obtained than when H_2O_2 is added at the beginning of the reaction. At higher content (1.5 eq. of H_2O_2), the reaction may be drastically affected by the presence of a large aqueous phase when H_2O_2 was added in one time. To confirm this hypothesis, H_2O_2 (1.5 eq.) was added dropwise and we were pleased to see that with a flow rate of $0.07 \text{ mL}\cdot\text{min}^{-1}$, 95% of MO was converted to 94% of MDHS, after 1 h of reaction (after the addition of H_2O_2) showing that if the amount of H_2O_2 is controlled, excellent yield of MDHS can be achieved.

Based on these results, we determine that an optimal molar ratio between hydrogen peroxide and the catalyst is required (around 550) to carry out this reaction in good yield with the addition of H_2O_2 in one time. It is known that Keggin-type $[\text{PW}_{12}\text{O}_{40}]^{3-}$ can be transformed to peroxy-active species, $\{\text{PO}_4[\text{W}(\text{O})(\text{O}_2)_2]_4\}^{3-}$ by an excess of hydrogen peroxide. It is a reversible redox reaction where phosphotungstic acid is generated after the oxidation of the desired substrate by peroxy-phosphotungstate anions (active form). Based on the literature a proposed catalytic mechanism for this reaction is shown in Scheme 2.

Scheme 2. Proposed mechanism of the oxidative reaction of methyl oleate in the presence phosphotungstic acid and hydrogen peroxide based on the literature.

According to the work of Noyori *et al.* and Strassner hydrogen peroxide is used to produce the peroxy-phosphotungstate anions that will react with MO in order to form a compound with tungsten that will lead to the formation of MDHS and the release of $[\text{PO}_4(\text{WO}_3)_{12}]^{3-}$ that can be converted again to peroxy-phosphotungstate anions.^{35,36} In order to prove that the epoxide was not an intermediate in this reaction, a complementary experiment was performed starting from epoxide instead of MO using 2.5 mmol of epoxide corresponding to a 55% conversion of MO after 30 min of reaction keeping similar amount of H_2O_2 and catalyst used in the conversion of MO (0.66 g of H_2O_2 and 0.075 g of catalyst). After 30 min, 60% of the epoxide was converted to various non

identified products with only 20% yield of MDHS formed. These poor yields clearly established that the epoxide can not be a significant intermediate in the dihydroxylation of OM studied herein. In the presence of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, the hydrolytic cleavage of epoxide was not the main route, and the mechanism of the reaction goes through a direct dihydroxylation of MO as described in the literature in the presence of tungstic acid.³⁷ The effect of the reaction temperature was then studied (Figure 4). When it was decreased from 80°C to 60°C , it logically took a longer time, namely 4 h instead of 2 h, to reach a similar conversion of MO (98% vs. 95%). A further decrease in the temperature to 40°C afforded poor MO conversions, the maximum observed being 20% (98% selectivity to MDHS) after 4 h of reaction.

Figure 4. Effect of the temperature on the conversion of methyl oleate using 1.1 eq. of H_2O_2 , 5 mmol of MO and 2 wt% of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (the yield of epoxide in all these experiments was less than 2%).

Interestingly, the increase of the reaction temperature to 100°C led to a decrease in the conversion of MO from 98% to 80% after 2 h of reaction. In fact, hydrogen peroxide is known to not be stable at this temperature and may be degraded, which may explain the decrease in MO conversion, by limiting the formation of the active species.³⁴ It can be pointed out that at 80°C , a MO conversion higher than 95% was achieved after the shortest of the explored reaction times (1 h) with 99% selectivity of MDHS.

With the optimized reaction conditions at 1.1 eq. of H_2O_2 , 2 wt% of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and 80°C , we wanted to explore catalyst recyclability. Unfortunately, phosphotungstic acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is a strong acid soluble under aqueous conditions, which leads to low pH around 1 under our conditions. After the reaction, it was thus impossible to simply recover an active form of the catalyst from the reaction medium. We thus explored the modification of this catalyst in order to obtain a heterogeneous catalyst. In the literature, Gharib *et al.* worked on the recycling of phosphotungstic acid by the substitution of hydrogen atoms by cesium ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$), using ultrasonic irradiation.³⁸ Inspired by this study, we synthesized $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$, which structure was confirmed by ICP analysis. The recycling of $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ was then performed using the optimal conditions previously described (1.1 eq. of H_2O_2 at 80°C).

However, in the presence of 2 wt% of $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ catalyst, only 40% of MO was converted with 39% of MDHS after 2 h of reaction. In order to improve the reaction rate in order to be competitive with the homogeneous form, the catalyst amount was optimized to achieve a high yield of MDHS after 2h of reaction. An increase of the catalyst loading from 2 to 6 wt% led to an increase of the MDHS yield from 39 to 79% (MO conversion of 80%) after 2 h of reaction. The catalyst recycling was then studied using these reaction conditions. To this aim, after each cycle, the reaction media was centrifuged, and the recovered catalyst was then washed several time with ethyl acetate and water, dried at 60 °C during 6 h and reused for the next cycle.

Figure 5. Recyclability of $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ using 5 mmol of MO, 1.1 eq. of hydrogen peroxide and 6 wt% of catalyst at 80 °C for 2 h.

The catalyst was recyclable up to 3 cycles without significant loss in MO conversion (76-80%) and yield (75-79%) in MDHS (Figure 5). After the third cycle, the conversion of MO and the yield of MDHS decreased.

In order to understand this loss of activity, $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ was characterized before reaction and after the first and 4th cycle. Elemental analysis of W and P was then performed on the $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ catalyst before and after recycling (Table 1). Elemental analysis showed no significant difference in phosphorus content before and after reaction while a clear difference was observed with tungsten measurements. Before recycling, $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ contained 63 wt% of W and after the fourth cycle, the weight percentage of W decreased from 63 to 56%. Thus activity loss was assigned to W leaching, which became too significant past the fourth cycle.

Table 1. Weight percentage of W and P measured by ICP in $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ before and after recycling.

Catalyst	W (wt%)	P (wt%)
Fresh $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$	63	0.9
$\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ after the 1 st run	63	0.9
$\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ after the 4 th run	56	0.8

XPS analysis were also conducted to analyze the surface of the catalyst and the results were compared to the result obtained from the characterizations of commercial $\text{H}_3\text{PW}_{12}\text{O}_{40}$ before (Figure 6) and after reaction (Figure 7).

Figure 6. XPS spectrum of W4f of commercial catalyst (left) and $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ before recycling (right).

XPS spectra of W4f of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ before recycling (Figure 6) showed 2 peaks at 36.4 eV and 38.5 eV corresponding to tungsten oxide WO_3 species of the $\text{PO}_4(\text{WO}_3)_{12}^{3-}$. $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ recovered after the first and the 4th cycle, contained two forms of tungsten oxide: WO_3 and WO_2 (at 35.1 eV) meaning that the catalyst was modified after reaction. The presence of WO_2 may have an impact on the recyclability process of the heterogeneous catalyst limiting the number of active species on the catalyst. However, the catalyst can be recyclable up to three cycles without using organic solvent or phase transfer agent.

Figure 7. XPS spectrum of W4f of $\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$ after the first cycle (left) and the 4th cycle (right).

Conclusions

Herein, we have demonstrated that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ can be used to selectively convert methyl oleate into methyl-9,10-dihydroxystearate (MDHS) with 99% yield. The yield to MDHS is higher than what was reported in the literature up to now (87%). The mechanism involved in this reaction was the direct dihydroxylation of MO. The active species were peroxo-

phosphotungstate anions formed in the presence of a certain amount of H_2O_2 that can be converted to phosphotungstate anions after the dihydroxylation of MO. It was shown that no organic solvent, no phase transfer agent was required during this reaction, but an appropriate molar H_2O_2 /catalyst ratio (around 550 in the optimized conditions) is needed to reach the highest yield to MDHS from MO. Hence, H_2O_2 concentration was 30%, and under this concentration phase transfer agent are often required. In the absence of phase transfer agent, high concentration of H_2O_2 are used which can lead to safety issue. In this study, by controlling the molar H_2O_2 /catalyst ratio, diols from MO were obtained with low concentrated solution of H_2O_2 and no additional organic solvent. Moreover, a recyclable form was synthesized ($\text{Cs}_{2.3}\text{H}_{0.7}\text{PW}_{12}\text{O}_{40}$) and was successfully recycled up to three cycles without significant loss in the catalytic performances.

Conflicts of interest

There are no conflicts to declare.

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