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TiO_2 (Anatase) Nanoparticles a Novel Catalyst for Synthesis of *vic*-Diacetates as Biologically Active Compounds

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Abstract

Introduction: This study represents efficient ring opening of epoxides to the corresponding vicinal diacetates in the presence of acetic anhydride. Different catalyst including molecular sieves, zirconyl triflate, $LiClO_4$, zeolite, $LiAlH_4$ and some other catalyst were reported so far as efficient catalyst for epoxide ring opening and subsequent diacetylation. In the present study, catalytic amount of commercially available TiO_2 (anatase) nanoparticles (NPs) were used to promote reactions.

Materials and Methods: According to X-ray diffraction (XRD) patterns, anatase is the main phase of the TiO_2 and scanning electron microscope (SEM)images revealed almost all the particles are under 100 nm in size. Existence of just oxygen and titanium peaks in EDS spectrum confirms high purity of catalyst.

Results: It was found that catalyst revealed good reusability and could be used in 3 cycles without marked loss of efficiency for synthesis of *vic*-diacetates from epoxides. Reactions of structurally diverse epoxides in the presence of acetic anhydride and catalytic amount of titanium dioxide were set at 100°C, progress of the reactions were monitored by thin layer chromatography (TLC) and gas chromatography (GC) which resulted in good to excellent yields.

Conclusions: In brief, the current work represents an efficient procedure for one-pot conversion of structurally different epoxides to the corresponding *vic*-diacetates. Comparison of cyclohexene oxide acetylation in the presence of titanium dioxide NPs and other catalyst confirmed acceptable efficiency of anatase titanium dioxide as a clean, safe and low cost catalyst for reaction promotion.

Keywords: Ring Opening, TiO_2 (Anatase) NP, *vic*-Diacetate

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Introduction

The popularity of epoxides is both due to their ability in forming applicable intermediates and their roles as a building block in organic synthesis. Epoxides have a great tendency for further derivatization,[1] thus can readily react with halides, carbon, nitrogen, oxygen or sulfur nucleophiles leading to a variety of outcomes and various functional groups such as alcohols, diols, aldehydes, alkanes, alkenes and ketones.

Because of the ring strain and intrinsic reactivity of the epoxides ring, these compounds are valuable intermediates in the production of high-value chemicals like pharmaceuticals. Reaction of epoxides with various nucleophiles can afford 1,2-difunctional products. Among these, 1,2-diols and vicinal diacetates possess valuable synthetic utilities. They are among the most important precursor for a wide range of biologically active natural and synthetic products.[2]

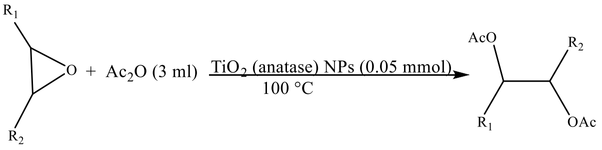
Generally, nucleophilic ring opening of epoxides leads to 1,2-diol products, and the subsequent acetylation provides *vic*-diacetates. Due to simplicity and higher yields of one-pot procedures, more attention is focused on the synthesis of *vic*-diacetates in one step and in the presence of various catalyst. There are different reports on conversion of epoxides to *vic*-diacetates in the presence of various types of catalysts naming erbium (III) triflate,[3] 4 Å molecular sieves,[4] ammonium-12-molybdophosphate,[5] zirconyl triflate,[6] phosphomolybdic acid with and without silica gel support,[7] $LiClO_4$,[8] Bu_3P,[9] zeolite[10] and $NaBH_4$, $LiAlH_4$, CaH_2 hydride transfer agent.[11]

To the best of our knowledge there is no report on epoxide conversion to *vic*-diacetates involving TiO_2 (anatase) nanoparticles (NPs), while it has been applied as catalyst for conversion of epoxides to β-amino alcohols[12] and also in various reactions including sulphur oxidation,[13] Hantzsch esters synthesis,[14] oxindole derivatives synthesis,[15] hydrogen production,[16] carboxymethylation and methylation of bisphenol A[17] and also dye degradation by polymer, and metal ion modified titanium dioxide.[16,18-21]

Nanocrystalline TiO_2 has also been applied as solid support for deposition of different catalyst acting as a carrier for metals and metal oxides.[22,23] Due to different advantages of this nanostructure, it can be considered as an efficient catalyst in ring opening of epoxides to *vic*-diacetates. It is one of the transition metal oxides and a promising semiconductor that exists in 3 crystalline forms; anatase, rutile and brookite, with band gaps of 3.2, 3.02, and 2.96 eV respectively. Rutile phase is the most thermally stable among the 3 phases, Brookite and anatase experience a phase transformation and convert into the rutile phase above 600°C.[24,25]

Due to high physical and chemical stability of TiO_2 in alkaline and acidic conditions, this semiconductor is widely researched.[26] Titanium dioxide can be utilized in several fields, including solar cells, photocatalyst, sensors, and self-cleaning.[27,28]

In this context, we report one-pot procedure for conversion of epoxides to corresponding *vic*-diacetates catalyzed by nano-sized titanium dioxide (anatase). Although TiO_2 is extensively applied in photo-induced and degradation reactions, due to its advantages including rather low-cost, photo stability, reusability, non-toxicity, which can be in accord with green chemistry principles, as well as its high stability in alkaline and acidic medium and high surface area, it was selected as heterogeneous catalyst for conversion of epoxides to the corresponding *vic*-diacetates in the presence of acetic anhydride (Scheme 1).



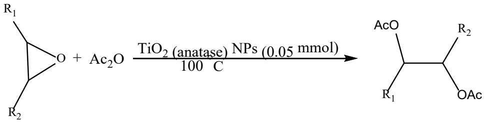
Scheme 1. TiO_2 (Anatase) NPs Catalyzed Synthesis of *vic*-Diacetates.

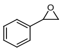
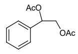
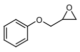
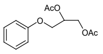
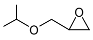
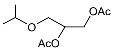
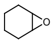
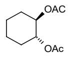
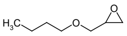
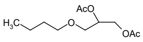
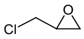
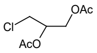
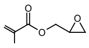
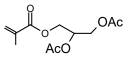
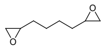
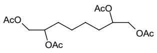
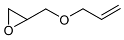
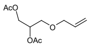
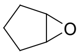
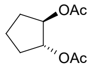
Materials and Methods

All the chemicals and reagents were purchased from Merck and Fluka companies and were used without further purification. The purity determination of the substrates and progress of reactions was monitored by a thin layer chromatography (TLC) on silica gel polygram SILG/UV 254 plates and gas chromatography (GC) Varian CP-3800 with FID detector and capillary column. Scanning electron microscope (SEM) was performed with a PHILIP XL-30, operated at 30 kV. X-ray diffraction (XRD) was conducted on a Philips Analytical XPERT diffractometer using a Cu Kα radiation (λ = 1.54056 A°) with a MINIPROP detector and operating at 40 kV and 40 mA. NMR and FT-IR spectra were recorded with Bruker 250 MHz and Bruker Vector 22 instrument respectively.

Generally, for synthesis of *vic*-diacetates in the presence of TiO_2 nanoparticles in a round-bottomed flask (25 mL), 0.05 mmol TiO_2 NPs was added to a solution of epoxide (1 mmol) and acetic anhydride (3 mL) and the reaction mixture was stirred in 100°C oil bath. The progress of the reactions was monitored by TLC and GC. After desired time (Table 1), an aqueous solution of NaOH (5%) was added to the mixture, and stirring continued for additional 10 minutes. The mixture was then extracted with ethylacetate (2 × 15 mL) and organic layers were dried over sodium sulfate. After removal of the solvents by rotary evaporator, the as obtained 1,2-acetyldiols were identified by the available techniques.

Table 1. Reaction of Epoxides to Vicinal Diacetates With Nano Titanium Dioxides in Acetic Anhydride



Entry	Epoxide (a)	Product (b)	Time (h:min)	Conversion (%)[a]	Yield (%)[b]
1			2	98.5	92
2			3	97	89
3			3:30	95	90
4			2:45	99	88
5			3:15	98.5	88
6			2	97	86
7			2:20	99	90
8			4	98	92
9			3:30	97.5	93
10			2:30	98	89

[a] Conversion is reported according to GC results. [b] Yields refer to isolated pure products.

Ethical Considerations

This study was approved by the Zanjan University Ethics Committee.

Results

FTIR Analysis

This analysis is used to confirm functional groups in desired structure. In Fourier-transform infrared spectroscopy (FTIR) of TiO_2 nano powder (Figure 1), Broad peak at 3356 cm^{-1} and a sharp peak at 1617 cm^{-1} are related to stretching vibrations of O-H and bending vibrations of adsorbed water molecules respectively. The broad intense peak at 903.79 cm^{-1} is also due to Ti-O-Ti vibration.[26]

XRD Analysis

The crystal structure of the titanium dioxide NPs was also characterized by XRD measurement. Figure 2 shows the XRD pattern of TiO_2 nano powder. The sharp peaks at 25, 39, 49, 55, 63 and 70 confirm the existence of anatase phase as the major phase, which coincides with JCPD 89-4921 standard.

SEM and EDS Analysis

SEM analysis was used to characterize general morphology and Size distribution of TiO_2 NPs. The SEM image reveals the spherical shape of TiO_2 nano powder with less than 100 nm in size (Figure 3). EDS spectrums of the TiO_2 is shown in Figure 4. This technique is used for quantitative analysis of the samples, in fact existence of expected atoms can be confirmed by EDS mapping. In EDS elemental spectra of titanium dioxides only titanium and oxygen peaks exist, which confirms high purity of titanium dioxide NPs.

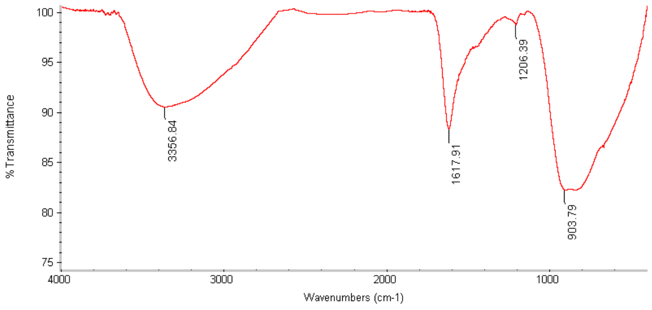


Figure 1. FTIR Spectra of TiO_2 NPs.

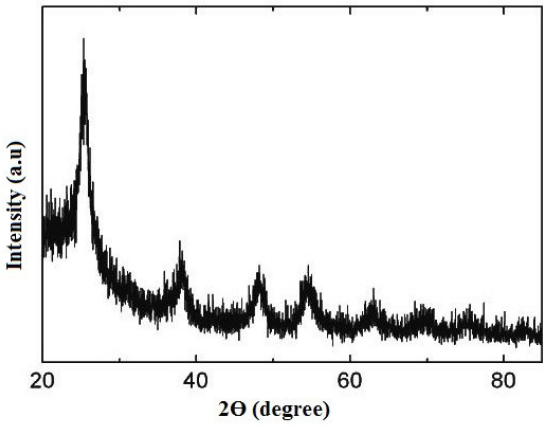


Figure 2. XRD Patterns of TiO_2 Nano Powder.

Epoxides Ring Opening in the Presence of TiO2 NPs and Acetic Anhydride

A variety of epoxides with diverse structures and different functional groups were selected and almost all the products were formed in high yields, in less than 4 hours (Table 1). In a typical procedure, the ring opening different types of epoxides (1 mmol) were achieved in the presence of TiO_2 (anatase) NPs (0.05 mmol) and acetic anhydride (3 mL). All the reactions were set at 100°C and the desired vicinal diacetates products were obtained in 88%-92% yields and the color of almost all the products were in pale yellow. The progress of the reactions was monitored by TLC and GC chromatography was applied for isolation of product. In order to show the effect of TiO_2 surface in catalytic reactions,[12] applied native TiO_2 and hexadecyltrimethoxysilane modified titanium dioxide in ring opening of epoxides.

The spectral data of synthesized vicinal diacetates are given below.

1,2-Diacetoxy-1-phenylethane (1b)

^{1}HNMR (250 MHz, CDCl3): δ = 2.02 (s, 3H), 2.05 (s, 3H), 4.25-4.45 (m, 2H), 5.96-6.15 (dd, *J*= 4.2, 7.8 Hz, 1H), 7.23-7.46 (m, 5H); ^{13}C NMR (63 MHz, CDCl3): δ = 20.83, 21.05, 66.08, 73.32, 126.93, 128.39, 129.01, 136.22, 170.00, 170.58; IR (cm^{-1}): 3033, 2954,1744, 1604, 1455, 1372, 1241, 1046, 1012, 950.

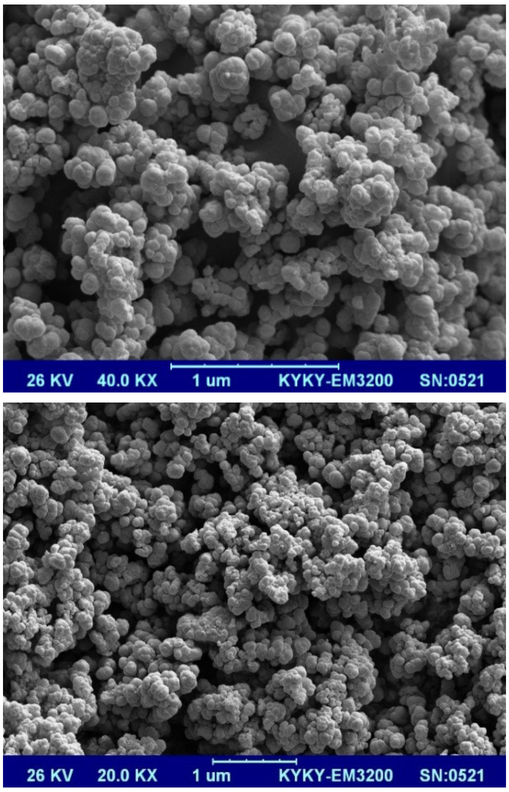


Figure 3. SEM images of TiO_2 NPs

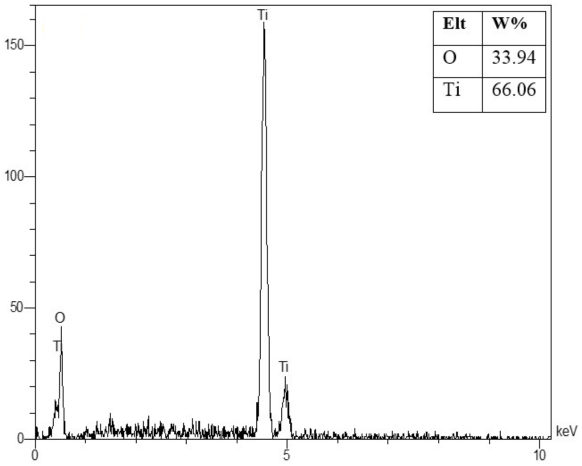


Figure 4. EDS Spectrum of TiO_2 NPs.

Vicinal diacetoxy-3-phenoxypropane (2b)

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm): 7.32–7.25 (m, 2H), 6.99–6.89 (m, 3H), 5.41–5.34 (m, 1H), 4.43 (dd, J 3.9, 12 Hz, 1H), 4.29 (dd, J 6, 12 Hz, 1H), 4.11 (d, J 5.1 Hz, 2H), 2.09 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ (ppm): 170.57, 170.26, 158.53, 129.27, 121.36, 114.59, 69.76, 65.96, 62.54, 20.92, 20.70; IR (cm^{-1}): 3041, 2957, 1746, 1600, 1588, 1497, 1371, 1228, 1050.

Vicinal diacetoxy-3-isopropoxypropane (3b)

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 5.15–4.96 (m, 1H), 4.28 (dd, J 3.6, 12 Hz, 1H), 4.12 (dd, J 3, 12 Hz, 1H), 3.58–3.40 (m, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.09 (d, J 6 Hz, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ (ppm): 170.68, 170.34, 72.32, 70.59, 66.12, 63.00, 21.91, 21.84, 21.00, 20.74; IR (cm^{-1}): 2918, 2849, 1743, 1463, 1371, 1229, 1118, 1047.

Vicinal diacetoxycyclohexane (4b)

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 4.79–4.5(m, 2H), 1.94 (s, 3H), 1.93 (s, 3H), 1.69–1.62 (m, 4H),1.36–1.16 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) δ (ppm): 172.31, 73.49, 30.16, 23.25, 21.17; IR (cm^{1-}): 2942, 2866, 1739, 1452,1368, 1251, 1042.

1,2-Diacetoxyhexane (5b)

^{1}H NMR (250 MHz, CDCl3): δ = 0.85 (t, 3H), 1.48-1.51(m, 2H), 1.53-1.55 (m, 2H), 2.04 (s, 3H), 2.06 (s, 3H), 3.35-3.42 (m, 2H), 4.10-4.33 (m, 2H), 5.12-5.16 (m, 1H); ^{13}C NMR (63 MHz, CDCl3): δ = 13.81, 19.15, 20.72, 20.99, 31.53, 62.92, 68.79, 70.27, 170.32, 170.64; IR (cm^{-1}): 2960, 2873, 1746, 1459, 1372, 1225, 1120, 1049, 961, 896, 843.

Vicinal diacetoxy-3-chloropropane (6b)

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 5.25–5.13 (m, 1H), 4.37–4.1 (m, 2H), 3.75–3.55 (m, 2H), 2.09 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ (ppm): 170.49, 170.41, 70.39, 62.36, 42.10, 20.86, 20.79; IR (cm^{-1}): 2963, 1744, 1436, 1371, 1221, 1046.

(2,3- Diacetoxy propyl) Methacr ylate (7b)

^{1}H NMR (CDCl3, 250 MHz) d 6.10–6.04 (m, 1H), 5.55–5.54 (m, 1H), 5.30–5.16 (m, 1H), 4.33–4.05 (m, 4H), 2.02 (s, 3H), 2.00 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (CDCl3, 63 MHz) d 170.41, 170.03, 166.66, 135.65, 126.37, 69.28, 62.39, 62.23, 20.76, 20.57, 18.13; IR (cm^{-1}): 2988, 2880, 1720, 1638, 1453, 1372, 1320, 1296, 1166, 1077, 1055.

Bis (3,4- diacetoxybuthane) (8 b)

1H NMR (250 MHz, CDCl3) δ (ppm): 1.27-1.43 (4H, 1.35 (tt, *J* = 7.4, 7.0 Hz), 1.35 (tt, *J* = 7.4, 7.0 Hz)), 1.46-1.58 (4H, 1.52 (td, *J* = 7.4, 7.1 Hz), 1.52 (td, *J* = 7.4, 7.1 Hz)), 2.05-2.06 (12H, 2.06 (s), 2.05 (s)), 4.40-4.44 (4H, 4.42 (d, *J* = 7.2 Hz), 4.42 (d, *J* = 7.2 Hz)), 4.74 (2H, tt, *J* = 7.2, 7.1 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ (ppm): 170.6, 75.2, 65.9, 21.0.

Vicinal diacetoxy-3-allyloxypropane (9b)

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 5.92–5.76 (m, 1H), 5.27 (dd, J 1.5, 17.4 Hz, 2H), 5.21 (dd, J 3, 17.4, 1H), 5.20–5.12 (m, 1H), 4.32 (dd, J 3.9, 12 Hz, 1H), 4.15 (dd, J 6.3, 12 Hz, 1H), 4.05–3.91 (m, 2H), 3.55 (d, J 5.1 Hz, 2H), 2.07 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ (ppm): 172.08, 172.16, 132.12, 119.03, 71.09, 70.21, 69.87, 62.80, 20.94, 20.67; IR (cm^{-1}): 2957, 2868, 1743, 1433, 1372, 1225, 1092, 1048.

Vicinal diacetoxycyclopantane (10 b)

1H NMR (250 MHz, CDCl3) δ (ppm):1.59-1.76 (2H, 1.70 (dtt, *J* = 13.4, 5.4, 1.4 Hz), 1.67 (dtt, *J* = 13.4, 9.4, 5.3 Hz)), 1.80-1.96 (4H, 1.88 (dddd, *J* = 9.4, 8.2, 7.6, 5.4 Hz), 1.90 (dddd, *J* = 8.2, 7.0, 5.3, 1.4 Hz)), 2.06 (6H, s), 5.16 (2H, ddd, *J* = 8.1, 7.6, 7.0 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ (ppm): 75.6, 24, 32.7, 21, 16.9.

Discussion

The results revealed that modified titanium dioxide led to fewer yields, which can be due to the steric hindrance and blocking the contact between the reactants and TiO_2 surface. The results confirm the important role of titanium dioxide surface in gaining higher yields, so in the current study in order to increase active surface area, nano-sized titanium dioxide was selected and no modification was made. Analysis of the product obtained from cyclohexene oxide and cyclopantene oxide acetic anhydride in the presence of acetic anhydride and TiO_2 NPs catalyst resulted in exclusively the corresponding trans-*vic*-diacetates (Table 1- entry 4, 10). In large-scale operations and an industrial point of view, catalyst reusability is of great importance. Since titanium dioxide can be separated from the reaction mixture by centrifugation, reusability of the catalyst was investigated in four cycles. The yields obtained from the recovered catalyst, revealed negligible loss of catalytic ability of TiO_2 NPs after 3 cycles. For example, the reaction of cyclohexene oxide with acetic anhydride Cause the synthesis of product vicinal diacetates cyclohexane in 99%, 98% and 98%, according to GC results. Increasing the number of recoveries causes tangible decrease in yields, which can be due to aggregation of TiO_2 NPs and loss of surface area. TiO_2 (anatase) NPs is able to afford *vic*-diacetates in better yields and lower catalyst amounts than the most efficient reported method (Table 2).

Conclusions

In brief, the current work represents an efficient procedure for one-pot conversion of structurally different epoxides to the corresponding *vic*-diacetates. Commercially available TiO_2 (anatase) NPs, a rather cheap, heterogeneous, non-explosive and environmentally benign catalyst was applied to

Table 2. Effect of Acetylation of Cyclohexene Oxide in the Presence TiO_2 NPs and Other Catalyst

Entry	Catalyst	Time (h)	Temp. (°C)	Solvent	Catalyst (mol %)	Product (%)	Ref.
1	$Er(OTf)_3$	3	r.t.	Ac_2O	0.1	93	1
2	AMP	1	r.t.	Ac_2O	10	93	3
3	$ZrO(OTf)_2$	0.5	50	Ac_2O	0.75	93	4
4	PBu_3	24	110	Toluene	10	92	7
5	Zeolite HY	10	25	Ac_2O	0.5	85	8
6	$NaBH_4$	1.5	Reflux	Ac_2O	0.2 mmol	95	9
7	-	18	Reflux	AcOH	-	45	29
8	$NaOAc.3H_2O$	2	70-80	Ac_2O	2 mmol	91	30
9	TiO_2 NPs	2.45	100	Ac_2O	0.05 mmol	99	Present work

promote the reactions. Reaction of different epoxides was set in the presence of catalytic amount of nano titanium dioxide and acetic anhydride in oil bath (100°C). Simple and mild reaction conditions, easy catalyst recovery, high yields and rather short reaction time, are considered as advantages of present protocol.

Authors' Contributions

RK and MTM have contributed to all experiments and has been supervised by FP. MTM has participated in the statistical analysis and in the preparation of the manuscript. All authors read and approved the final manuscript.

Conflict of Interest Disclosures

The authors declare they have no conflicts of interest.

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