

SO₄²⁻/SnO₂-Catalyzed efficient one-pot synthesis of 7,8-Dihydro-2H-Chromen-5-ones by formal [3+3] cycloaddition and 1,8-Dioxo-octahydroxanthenes via a Knoevenagel condensation

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Abstract: SO₄²⁻/SnO₂-Catalyzed efficient one-pot synthesis of 7,8-dihydro-2H-chromen-5-ones by formal [3+3] cycloaddition and 1,8-dioxo-octahydroxanthenes via a Knoevenagel condensation is described with good yields under mild reaction conditions. The catalyst could be reused several times without losing its catalytic efficiency.

Keywords: cat. SO₄²⁻/SnO₂; α,β -unsaturated aldehydes; cyclic 1,3-diketones; Knoevenagel condensation; reusability.

1. Introduction

Synthesis of xanthenediones is a continuing hot topic because these moieties are privileged pharmacophores as well as valuable reactive intermediates for both synthetic and medicinal chemists¹. Furthermore, these compounds can be used as dyes², in laser technologies³, and as pH sensitive fluorescent materials for visualization of biomolecules⁴. In addition, substituted xanthenes are structural key-units in several natural products⁵.

Many procedures exist for the synthesis of 1,8-dioxo-xanthenes involving InCl₃/P₂O₅⁶, [Hbm]BF₄/ultrasound⁷, silica-bonded S-sulfonic acid⁸, PMA.SiO₂⁹, *p*-dodecylbenzenesulfonic acid¹⁰, amberlyst-15¹¹, SmCl₃¹², Fe₃O₄ nanoparticles¹³, PEG-6000¹⁴, molecular iodine¹⁵, cat. H₂SO₄¹⁶, ZrOCl₂·8H₂O¹⁷, *p*-TSA¹⁸, [bmim]HSO₄¹⁹, Fe(HSO₄)₃²⁰, diammonium hydrogen phosphate²¹, etc. However, many of these methods include strong acidic reaction conditions, low yields, long reaction times, high temperatures or they are dedicated only to the application of aromatic aldehydes, use of toxic and costly reagents/catalysts, complex workup procedures, etc. Moreover, the recovery of the catalyst is also a problem.

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2*H*-Pyran motif has got variety of interesting biological activities and also in photochromic materials.²²⁻²³ 2*H*-Pyrans were prepared using piperidine²⁴, BF₃.H₂O²⁵, PPTS²⁶, PPA²⁶, InCl₃²⁷, In(OTf)₃²⁵, TiCl₄²⁵, I₂²⁸, phosphoric acid as a Brønsted catalyst²⁹, etc. Although several synthetic approaches for construction of 2*H*-pPyran derivatives have been reported, more simple, cost-effective and reusable approaches are still in demand because of their importance.

The substitution of homogeneous liquid acids by heterogeneous solid superacids as catalysts is expected to ease their separation from reaction mixture, less corrosion, allowing continuous operation as well as regeneration and neutralization of the catalyst and lowering the cost of process installation and maintenance.³⁰⁻³¹ Sulfated metal oxides with both Brønsted and Lewis acid sites are widely used as solid super acid catalysts.³²⁻³³ Sulfated metal oxides are stable to moisture, air and heat. They are easy to prepare and environmentally benign.³⁴

In past few years, considerable attention has been given to sulphated tin oxide (hereafter, STO) which is known to possess strongest surface acidic sites.³⁵ STO was found to be efficient and suitable in effecting several organic transformations.³⁶ The catalyst can be repeatedly used without sacrificing its catalytic activity, thus rendering heterogeneous character. Moreover, to our knowledge, STO has not yet been explored as a catalyst for the synthesis of xanthenediones and chromenones.

In continuation of our interest in developing novel synthetic methodologies, particularly carbon-carbon, carbon-heteroatom bond formations to synthesize pharmaceutically relevant heterocycles,³⁷ herein we report our findings for a highly efficient method for the synthesis of 7,8-dihydro-2*H*-chromen-5-ones and 1,8-dioxo-octahydroxanthenes, respectively (see Tables 1-3).

2. Results and discussion

(a) *Synthesis of 7,8-Dihydro-2H-Chromen-5(6H)-ones*: 1,3-dicarbonyl compounds can be condensed to α,β -unsaturated aldehydes to form a 2*H*-pyran motif via a formal [3+3] cycloaddition.³⁸ From a synthetic point of view, this type of approach allows the formation of multiple bonds, rings. Initially, the selected model reaction was carried out with 1,3-cyclohexane-dione (1 mmol, **1a**) and crotonaldehyde (1.1 mmol, **2**) in the presence of 10 mol% STO at 70 °C (Figure 1.). Herein, the reaction temperature was crucial in terms of the reaction rate and product yield. The above model reaction was carried out at different temperatures (RT, 50, 70 and 100 °C) with 10 mol % of catalyst loading separately.

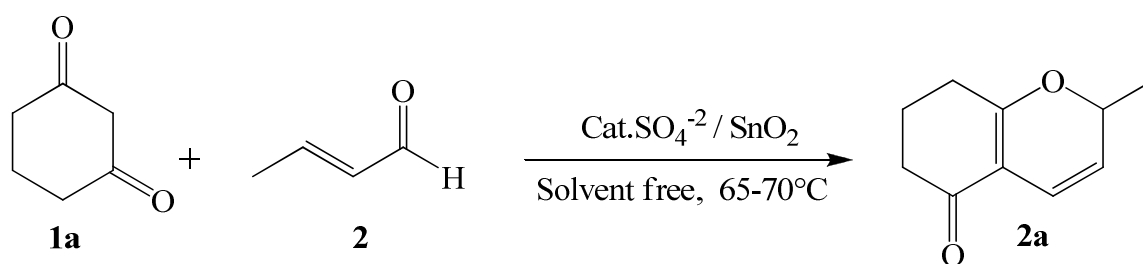


Figure 1. SO₄²⁻/SnO₂-Catalyzed Synthesis of 7,8-Dihydro-2*H*-Chromene-5(6*H*)-ones

It was found that the desired compound **2a** was obtained in excellent yield at 65-70 °C. Further increase of the temperature (100 °C) neither increased the yield nor shortened the reaction time (Table 1, entry 10).

We examined several organic solvents such as acetic acid (82%), toluene (68%), methanol (0%), acetonitrile (0%), isopropyl alcohol (0%) (which are commercially available and used without further purification or drying) for the test reaction. Surprisingly, when the reaction was carried out under solvent-free conditions, the product was formed in excellent yield (85%), compared to the solvents tested (see Table 1, entry 7). The formation of **2a** was readily confirmed by the observation of carbonyl absorption of enone in the IR spectrum at 1645 cm⁻¹ and the expected chemical shifts associated with two olefinic protons on 2*H*-pyran ring at δ 6.43 Hz (d, *J*=10.0 Hz, 1H) and 5.26 (dd,

$J=10.0$ Hz, 2.6 Hz, 1H) ppm in the ¹H NMR spectrum. Mass spectral analysis showing m/z (rel. abund.%) 165.1 ([$M+1$]⁺, 100), further proves the formation of **2a**. No xanthene derivative was obtained in this case. When aromatic α,β -unsaturated aldehydes employed as substrates, corresponding chromenones were formed in negligible amounts.

Table1. Screening for the reaction conditions^a

Entry	Cat. (mol%) ^a	Solvent	Temp (°C)	Time min)	Yield ^b (%)
1	10	MeOH	65-70	60	0
2	10	CH ₃ CN	65-70	60	0
3	10	IPA	65-70	60	0
4	10	Toluene	65-70	60	68
5	10	AcOH	65-70	60	82
6	5	Neat	65-70	60	48
7	10	Neat	65-70	45	85/83 ^c
8	20	Neat	65-70	45	85
9	0	Neat	65-70	24 h	0
10	10	Neat	100	60	85

^a1.0 mmol **1a**, 1.1 mmol **2**, cat. SO₄²⁻/SnO₂.

^bIsolated yield.

^cYield after 3rd recycle.

To determine the role of the catalyst, the same reaction was carried out in the absence of catalyst and only starting materials were isolated from the reaction mixture even after 24 h. It indicates that the catalyst exhibits high catalytic activity in this transformation. In order to evaluate the most appropriate catalyst loading, the test reaction using crotonaldehyde and 1,3-cyclohexanedione (molar ratio: 1.1:1) was carried out using 5, 10, 15, and 20 mol% of catalyst under solvent-free conditions (Table 1, entries 6-8). It was found that 10 mol % of catalyst showed maximum yield in minimum time at 70°C (Figure 1. and Table 1, entry 7). Increasing the used catalyst further did not affect the yield (Table 1, entry 8). The efficiency of the catalyst was found to be good even after three cycles with a minimum variation of the yields of the products (83%). After filtration from reaction mixture, the catalyst was reactivated by heat treatment at 400-500 °C for 1 h in an oven under air atmosphere and then reused.

With optimized reaction parameters in hand (10 mol% of STO, solvent-free conditions at 65-70 °C), we extended this methodology to various reactive aliphatic α,β -unsaturated aldehydes such as 2-methylbutenal, 4-methylpentenal, 2-methylpentenal, *trans*-2-hexenal with 1,3-cyclohexanedione (**1a**) and dimedone (**1b**), respectively, to afford corresponding chromenone derivatives within 45-90 min (Table 2, entries 1-10). This is a mild protocol for such an annulation reaction and consistently gives the corresponding products in moderate to good yields. Very recently, we have successfully synthesized pyranocoumarin using 4-hydroxycoumarin with prenyl acetate *via* *O*-acylation followed by ring annulation.³⁹

(b) *Synthesis of 1,8-dioxo-octahydroxanthenes*: Encouraged by these results, we extended the scope of STO catalyzed annulation for the synthesis of 1,8-dioxo-octahydroxanthenes using 2:1 molar ratio of aldehydes and diketones. Initially, the synthesis of **7a** from cinnamaldehyde **7** and 1,3-cyclohexane-dione (**1a**) using STO was studied as model reaction under solvent-free conditions at varying temperatures (RT, 70, 100 and 120 °C) with 10 mol% STO. It was found that desired compound **7a** was obtained in moderate yield (52%) at 120 °C under solvent free conditions. Acetic acid proved to be the best solvent among the chosen solvents from Table 1, for the formation of desired xanthenes (Figure 2).

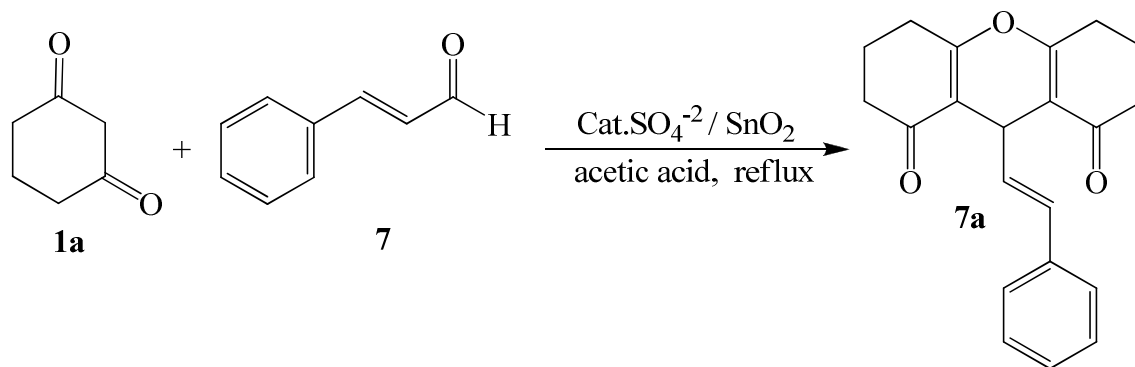


Figure 2. $\text{SO}_4^{2-}/\text{SnO}_2$ -Catalyzed Synthesis of 1,8-Dihydro-octahydroxanthenes

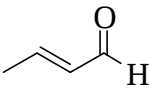
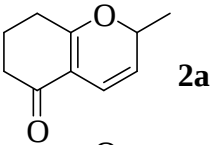
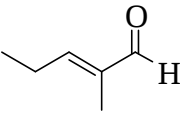
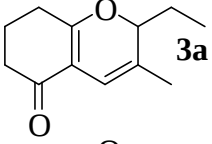
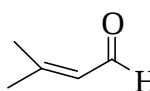
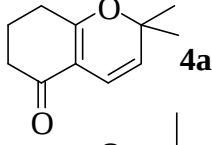
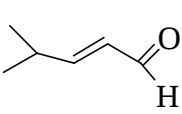
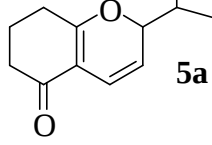
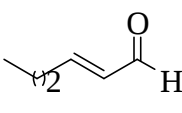
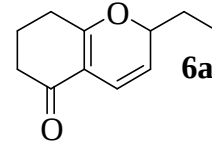
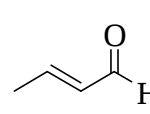
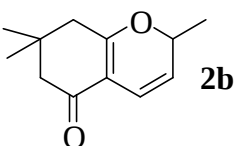
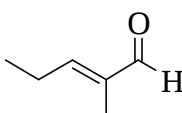
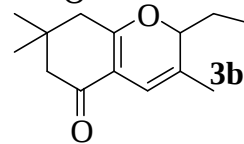
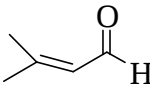
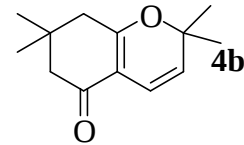
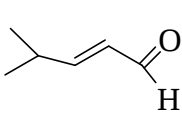
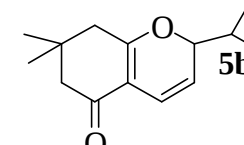
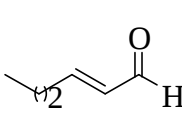
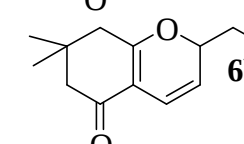
This protocol tolerates well with electronically divergent cinnamaldehydes containing both electron donating and electron-withdrawing substituents such as -OMe and -NO₂ using 1,3-cyclohexanedione (**1a**), 5,5-dimethyl 1,3-cyclohexanedione (**1b**) and 5-Phenyl-1,3-cyclohexanedione (**1c**) respectively (Table 3, entries 1-7).

5-Phenyl-1,3-cyclohexanedione (**1c**) also reacted well with cinnamaldehyde to give the corresponding xanthene in good yield (Table 3, entry 8). The conversion was complete within 4-5.5 h. In no case, we were able to detect Knoevenagel intermediate products. The structure of the products was established from their spectral data (IR, ¹H, ¹³C NMR and mass). The carbonyl group appear in the expected region around 194.7-197.5 ppm. The proton at the bridge between the two cyclohexanone rings appears as doublet in the region of 4.40-4.45 ppm and the bridge carbon appears around 40.83 ppm. The four methyl groups of the dimedone give rise to two close singlets each with six hydrogens at around 1.12 and 1.16 ppm, respectively forming two sets of axial and equatorial methyl groups. Recycling of catalyst was examined using the condensation reaction of cinnamaldehyde **7** and 1,3-cyclohexanone-dione (**1a**) in acetic acid under the optimized conditions. After the reaction was complete, the mixture was filtered and the remaining was washed with DCM, and the catalyst was reactivated at 400-500 °C, and reused in the next reaction. The recycled catalyst could be reused three times without any appreciable loss in the catalytic activity of STO (Table 3, entry 1).

Possible mechanism pathway might explain the formation of 7,8-dihydro-2*H*-chromen-5(6*H*)-one. Knoevenagel condensation between the enol derivative of the β-diketone and the electrophilic carbonyl of the α,β-unsaturated aldehydes might furnish oxa-intermediate, which might undergo a [3+3] electrocyclization to form the desired product (Figure 1). This condensation/electrocyclization might also occur through a *double activation of the catalyst* (STO), which can play both the role of a *Bronsted acid* (to activate the aldehydes *via* hydrogen bonding) and the role of *Lewis acid* (to activate the enol formation). Thus, the activation of both partners of this reaction by STO might explain the greater reactivity all along the catalytic process.

The formation of 1,8-dioxo-octahydroxanthene can be rationalized through the following sequence of events as shown in Figure 2. One molecule of diketone was firstly condensed with aldehyde which is activated by STO, to afford intermediate Knoevenagel product, **A**. Then the active methylene of the second molecule of diketone reacted with the Knoevenagel product *via* conjugate Michael addition to generate the intermediate **B**, which undergoes intramolecular cyclodehydration to give the desired product.

Table 2. Synthesis of 7,8-Dihydro-2H-Chromen-5(6H)-ones

Entry	Aldehyde	Product	Time	Yield (%) ^a
1	2 	 2a	45 min	85
2	3 	 3a	1 h	74
3	4 	 4a	45 min	80
4	5 	 5a	1 h	78
5	6 	 6a	1.5 h	64
6	2 	 2b	30 min	82
7	3 	 3b	1 h	84
8	4 	 4b	45 min	86
9	5 	 5b	1 h	74
10	6 	 6b	1.5 h	61

^aReaction conditions: diketone: 1 mmol, aldehyde: 1.1 mmol, STO: 10 mol%, solvent-free

^bIsolated yields after column chromatography.

Table 3. Synthesis of 1,8-dioxo-octahydroxanthenes^a

Entry	Aldehyde	Product	Time (h)	Yield (%) ^b
1			n=H (7a) 4	86/82/84 ^c
2	7		n=CH ₃ (7b) 4.5	84
3			8a 5	78
4			n=H (9a) 4	76
5	9		n=CH ₃ (9b) 4.5	75
6			n=H (10a) 4	83
7	10		n=CH ₃ (10b) 5	88
8			11c 5.5	75

^aReaction conditions: diketone: 2 mmol, aldehyde: 1 mmol, STO: 10 mol%, solvent-free^bIsolated yields after column chromatography.^cYield after 3rd recycle.

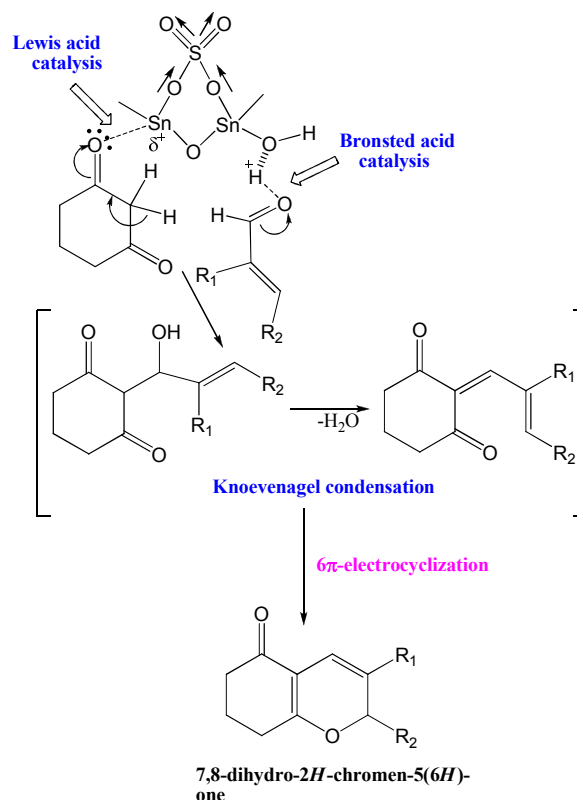


Figure 3. Possible formation mechanism of 7,8-dihydro-2H-chromen-5(6H)-one

3. Conclusion

In conclusion, we have developed sulfated tin oxide-catalyzed convenient and atom efficient protocol for the synthesis of 7,8-dihydro-2H-chromen-5-ones under neat conditions and 1,8-dioxo-octahydroxanthenes using acetic acid as solvent. The good yields, mild reaction conditions, easy isolation and purification, and easily preparable recyclable catalyst make the eco-friendly procedure an added attractive alternative to the existing methods.

4. Experimental

STO was prepared according to the literature report.³⁹ All melting points were determined on an Electrothermal Gallenkamp apparatus. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance Spectrometer 300 MHz. IR spectra were recorded on Nicolet Fourier Transform spectrometer. Mass spectra were obtained on a 7070H or VG Autospec Mass spectrometer. Thin-layer chromatography (TLC) was performed on GF-25U (Anal. Tech) plates and silica gel glass-backed plates. Routine column chromatography was conducted using silica gel 100-200 mesh.

General experimental procedure for the 7,8-dihydro-2H-chromen-5(6H)-ones (entries 1-10, Table 2): To a mixture 1,3-cyclohexanedione or dimedone (1.0 mmol) and aliphatic α,β -unsaturated aldehyde (1.1 mmol), sulphated tin oxide (0.1 mmol) was added and the reaction mixture under neat conditions was stirred for the specified time (see Table 2) at 65-70 °C. After completion of the reaction (monitored by TLC), to the reaction mixture was added methylene dichloride (5 mL). Catalyst was filtered and washed with methylene dichloride. The residue was purified by silica gel column with petroleum ether/ethyl acetate (1:3) as eluent to afford the corresponding 7,8-dihydro-2H-chromen-5(6H)-ones.

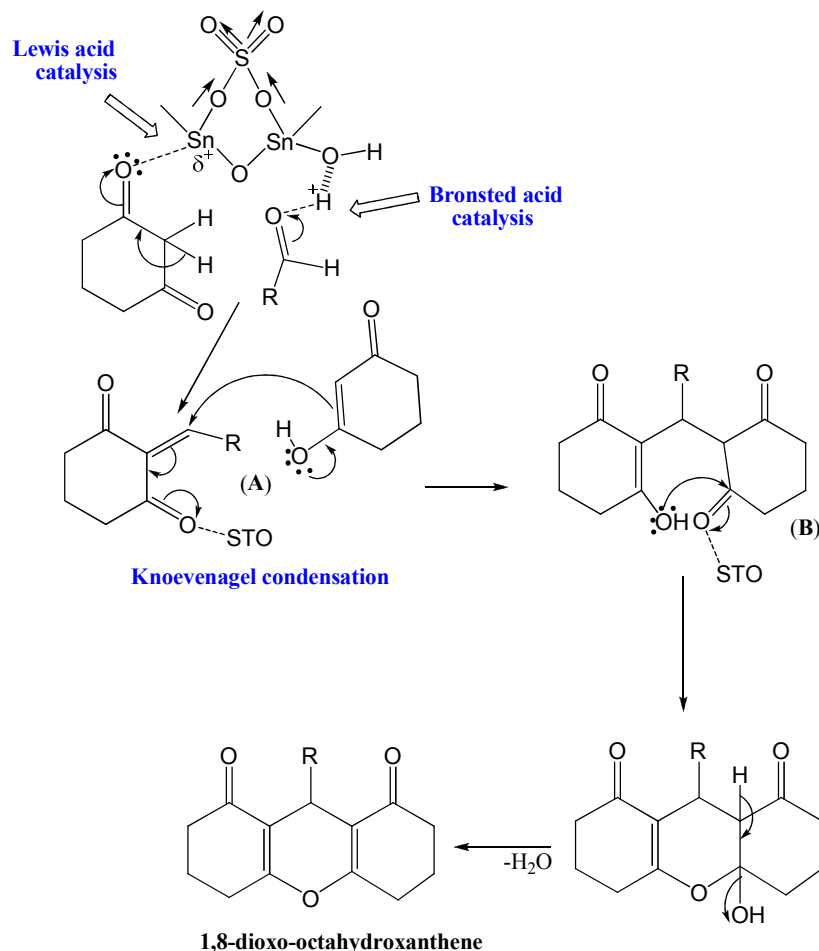


Figure 4. Possible formation mechanism of 1,8-dioxo-octahydroxanthene.

General experimental procedure for 1,8-dioxo-octahydroxanthenes (entries 1-8, Table 3): A mixture of 1,3-cyclohexanedione, dimedone or 5-phenyl-1,3- cyclohexanedione (2 mmol) and aromatic α,β -unsaturated aldehyde (1 mmol), sulfated tin oxide (0.1 mmol), acetic acid (5 mL) was added and the reaction mixture was heated at reflux temperature for the specified time (see Table 3). After completion of the reaction (monitored by TLC), the mixture was filtered to remove insoluble catalyst. The filtrate was cooled to 50 °C, distilled off completely under vacuum, cooled to room temperature. Water (5 mL) was added, neutralized using Na_2CO_3 and extracted with ethyl acetate (2x5 mL). The combined organic was dried over anhydrous Na_2SO_4 . The solvent was evaporated under vacuum to give the desired product, which was recrystallized from ethanol to afford the pure product or purified by column chromatography using silica 100-200 mesh.

Supporting Information

Supporting Information accompanies this paper on <http://www.acgpubs.org/OC>

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