

Synthesis, characterization, and crystal structures of α , α' -bis(substituted-benzylidene)cycloalkanone derivatives by nano-TiO₂/HOAc

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Abstract A new and economical synthesis of α , α' -bis(substituted-benzylidene)cycloalkanones has been achieved by the reaction of cycloalkanones with different aromatic aldehydes using nano-TiO₂/acetic acid as a catalyst in ethanol under reflux conditions with excellent yields. Five new products and three new single crystal structures are reported.

Keywords α , α' -bis(substituted-benzylidene)cycloalkanones \cdot Nano-TiO₂ \cdot Crystal structure

Introduction

In recent years, transition metal nanoparticles are used as efficient catalysts for various synthetic organic transformations due to their high surface area-to-volume ratio and coordination sites, which are mainly responsible for their catalytic activity [1, 2]. Titanium dioxide nanoparticles (nano-TiO₂) are certainly among the most interesting metal oxides that enable organic reactions to occur. It has been proved that nano-TiO₂ is an efficient catalyst for the synthesis of quinoxalines [3], β -acetamido ketones [4], 1,8-dioxo-octahydroxanthenes [5], dibenzo[a,j]xanthenes [6], and polyhydroquinolines [7]. Non-toxicity, easy availability, high activity, strong oxidizing power, reusability, and long-term stability are the main advantages of nano-TiO₂ [3, 8].

The α , α' -bis(substituted-benzylidene)cycloalkanones, as α , β -unsaturated carbonyl compounds are generally synthesized by Claisen–Schmidt condensation. This

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class of compound is known to have a broad spectrum of biological properties such as antimicrobial [9], anti-inflammatory [10], antimutagenic [11], antitumor [11], and antipyretic [12] activities. Moreover, they can be used in optics [13], rocket engineering [14], photolithography [15], and liquid crystalline polymers [16].

Generally, the synthetic approach to α , α' -bis(substituted-benzylidene)cycloalkanones involves Claisen–Schmidt condensation of cyclic ketones with two equivalents of aromatic aldehyde that is catalyzed by a strong base or an acid. Various catalysts, such as Lewis or Brønsted acids [17–19] or bases [20, 21], heterogeneous catalysts [22, 23], and complexes of metal ions [24, 25] under heating condition or sonication [26] or microwave irradiation [27, 28], have been reported for their synthesis in the literature which afford variable product yields.

A wide variety of application and considerable interest for crystallographic investigations on the α , α' -bis(substituted-benzylidene)cycloalkanones encouraged us to report new derivatives and also novel single crystal structures in order to determine the geometry of the cyclohexanone moiety. Herein, we have reported a new method for their synthesis by using nano-TiO₂/acetic acid as catalyst in ethanol under reflux conditions (Scheme 1). It is notable that acetic acid is beneficial to the catalytic activity of nano-TiO₂, which increases it significantly.

Results and discussion

Initially, nano-TiO₂ powder is easily prepared according to the reported procedure [29]. Figure 1a shows the XRD patterns of prepared nano-TiO₂ powder. As seen in Fig. 1a, the following peak signals from (101), (103), (004), (112), (200), (105), (211), (204), (220), (215), and (224) planes confirm the formation of anatase crystal phase mostly, which coincides with the JCPD 89-4921 standard. The size of the nano-TiO₂ powder was also determined by X-ray line width using the Scherrer formula given as $D = 0.9\lambda/\beta \cos\theta$, where D is the average crystalline size, λ is the X-ray wavelength used, β is the angular line width at half maximum intensity, and θ is the Bragg's angle. The average size of the nano-TiO₂ powder for $2\theta = 25.303^{\circ}$ was estimated to be around 21.88 nm. Transmission electron microscopy (TEM) analysis was used for characterization of nano-TiO₂ powder (Fig. 1b). The TEM image reveals the spherical nano-TiO₂ powder with an average size of 20–30 nm.

The FT-IR spectra of nano-TiO₂ powder is shown in Fig. 2. The bending vibrations of adsorbed water molecules and stretching vibrations of OH are around 1620–1635 and 3350–3450 cm⁻¹, respectively [30]. The broad intense band at 520



Scheme 1 New route for the synthesis of α , α' -bis(substituted-benzylidene)cycloalkanone derivatives



Fig. 1 a The X-ray diffraction patterns of the nano-TiO₂, b the TEM image of the nano-TiO₂



and 689 cm⁻¹ is due to Ti–O–Ti vibration, which is consistent with the reported IR spectra for nano-TiO₂ [30].

Thermo gravimetric analysis (TGA) of nano-TiO₂ is shown in Fig. 3. The TGA curve displays a weight loss (4 wt%) below 100 °C which corresponds to the loss of the physically adsorbed water. Also, there is a slight weight loss (1 wt%) between

100 and 800 °C, which possibly corresponds to the dehydroxylation of nano-TiO₂. Also, from the TGA, we understood that nano-TiO₂ has a great thermal stability (up 400 °C) confirming that it can be safely used in organic reactions at temperatures in the range of 80–150 °C.

Considering the researches toward evaluating the catalytic activity of nano-TiO₂ in chemical transformations, we have investigated the synthesis of α , α' -bis(substituted-benzylidene)cycloalkanones in the presence of nano-TiO₂ under heating conditions.

We have employed cyclohexanone (1 mmol) and benzaldehyde (2 mmol) as a representative model reaction in the presence of 20 mol% of nano-TiO₂. To choose the most appropriate condition in this condensation reaction and to understand the influence of different variables in this reaction, several experiments were studied. The results are summarized in Table 1.

As Table 1 shows, the best yield was obtained in refluxing ethanol (Table 1, entry 6), while other selected temperatures and solvents did not provide good condition for this reaction (Table 1, entries 1–5 and 7–9). It is notable that no product formed within a reasonable time in the absence of catalyst (Table 1, entry 10), and the optimum amount of the catalyst was 20 mol%, which is enough to carry out the reaction efficiently (Table 1, entry 6). Furthermore, the yield of the product by using bulk TiO₂ was not satisfactory in comparison to nano-TiO₂ (Table 1, entry 13). The high efficiency of the nano-TiO₂ may be due to its high surface area compared with the bulk TiO₂.

Considering the optimized reaction conditions (Table 1, entry 6), we have investigated the generality of this method with different aldehydes and ketones to prepare a series of α , α' -bis(substituted-benzylidene)cycloalkanones (Table 2).

As shown in Table 2, the aldehydes bearing both electron-donating and electronwithdrawing groups can be used in this reaction to afford desired products with high yields. Moreover, in the published papers, most attention has been given to five- and

Table 1 Optimum conditions for the synthesis of α , α' - bis(benzylidene)cyclohexanone	Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Yield ^a (%)
	1	Nano-TiO ₂ (20)	_	R.T	0
	2	Nano-TiO ₂ (20)	-	40	0
	3	Nano-TiO ₂ (20)	-	60	35
	4	Nano-TiO ₂ (20)	-	80	70
	5	Nano-TiO ₂ (20)	-	100	60
	6	Nano-TiO ₂ (20)	EtOH	80	93
	7	Nano-TiO ₂ (20)	H_2O	80	10
	8	Nano-TiO ₂ (20)	PEG	80	0
Reaction conditions: cyclohexanone (1 mmol), benzaldehyde (2 mmol), glacial AcOH 20 drops, reaction time: 6 h ^a Isolated yields	9	Nano-TiO ₂ (20)	CH ₃ CN	80	20
	10	Nano-TiO ₂ (0)	EtOH	80	0
	11	Nano-TiO ₂ (10)	EtOH	80	65
	12	Nano-TiO ₂ (30)	EtOH	80	90
	13	Bulk-TiO ₂ (20)	EtOH	80	45

Entry	Product	Time (h:min)	Yield ^c (%)	M.P. (°C)		
				Found	Reported	
1		6:10	91	188–190	188–189 [17]	
2		6:15	94	211–213	209–210 [17]	
3		6:00	94	240–242	239–241 [17]	
4 ^a		7:00	88	168–171	Not reported	
5		5:50	97	155–156	160–161 [17]	
6		5:30	97	227–229	230–231 [31]	
7	F 3n F	5:20	94	235–236	237–239 [28]	
8	o Br 3h Br	5:00	92	254–257	254–257 [28]	
9		6:00	94	117–119	113–115 [17]	
10		6:40	90	160–162	159–161 [17]	
11		6:15	92	167–169	163–165 [17]	
12	JR	7:30	85	156–158	155–157 [17]	

Table 2 Synthesis of α , α' -bis(substituted-benzylidene)cycloalkanone derivatives under optimized conditions (new compounds)

Entry	Product	Time (h:min)	Yield ^c (%)	M.P. (°C)	(°C)	
				Found	Reported	
13	Cl O Cl	6:10	96	101–103	102–106 [17]	
14 ^b		5:45	97	148–150	147–148 [31]	
15		5:45	95	157–159	154–156 [28]	
16	o Br	5:30	89	161–164	163–165 [17]	
17		5:50	93	209–211	208–211 [17]	
18 ^b		6:30	92	138–140	137–138 [32]	
19 ^a		8:00	83	208–211	Not reported	
20 ^a		6:10	92	181–183	Not reported	

Table 2 continued

Entry	Product	Time (h:min)	Yield ^c (%)	M.P. (°C)		
				Found	Reported	
21	H ₃ CO	7:00	93	170–172	171–172 [32]	
22		6:50	94	157–159	156–157 [32]	
23		6:00	98	175–178	177–178 [32]	
24 ^{a,b}	3w P	6:15	95	174–177	Not reported	
25 ^a	3x Br	5:50	87	186–189	Not reported	
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Table 2 continued

Reaction conditions: cycloalkanone (1 mmol), aldehyde (2 mmol), nano-TiO₂ (20 mol %), glacial AcOH 20 drops, EtOH (5 ml), reflux

- ^a New compounds
- ^b New single crystals

^c Isolated yields

six-membered carbocyclic ketones, while in this paper 4-(tert-butyl)cyclohexanone was involved in the reaction too (Table 2, entries 18–25).

All the products are identified by the comparison of their melting point data with those reported in the literature [17, 28, 31, 32] and some of them are characterized by FT-IR and NMR. In addition, new single crystals (compounds 3n, 3r, and 3x) are identified by X-ray crystallography (Fig. 4).



Fig. 4 Perspective view of the molecules 3n(a), 3r(b), and 3x(c); ellipsoids are drawn at 33 % (50 % for 3x) probability level, hydrogen atoms are shown as spheres of arbitrary radii. For 3r, only the more-occupied molecule is shown

In all the structures, the central ring is close to sofa conformation (as can be seen by the torsion angles values) with five atoms almost coplanar, and the sixth one, C4, significantly, by more than 0.7 Å out of this plane. Overall conformation of the molecule, which might be described by the dihedral angles between the terminal planar rings, is influenced by the presence/absence of the *t*-butyl substituent at the C4 atom. For **3n** (unsubstituted) the dihedral angles for the symmetry-independent molecules are over 20° [29.88(11)° for molecule A, 26.87(12)° for B], while for substituted **3r** and **3x** the angles are smaller, 7.5(3)°



Scheme 2 The plausible mechanism for the condensation reaction of cycloalkanones and aryl aldehydes in the presence of nano- $TiO_2/HOAc$

for **3r** and $10.52(7)^{\circ}$ for **3x**. In the crystal structures only weak C–H···O and π ··· π contacts can be identified as specific, and to some extent, directional intermolecular interactions.

The proposed mechanism for the formation of α , α' -bis(substituted-benzylidene)cycloalkanones is depicted (Scheme 2). Predominantly, the reaction proceeds via the enolate pathway, wherein ketone (I) is tautomerized to the enolate form (II) in the presence of acid. The enolate ion is very nucleophilic and attacks the electrophilic carbonyl group of aromatic aldehyde (III) which is activated by nano-TiO₂ as a Lewis acid, to form β -hydroxyketone (IV) followed by a dehydration step (V). The same nucleophilic addition occurs on the other side of ketone (VI) to obtain symmetric hydroxyketone (VII), followed by dehydration again to give the final cross-aldol condensation product (VIII).

Table 3 Crystal data, data collection and structure		3n	3r	3x
refinement	Formula	C20H16Cl2O	C ₂₄ H ₂₆ O	$C_{24}H_{24}F_2O$
	Formula weight	343.23	330.45	366.43
	Crystal system	Triclinic	Orthorhombic	Monoclinic
	Space group	P-1	Pca2 ₁	$P2_1/n$
	a (Å)	10.2167(5)	12.3099(6)	5.8770(10)
	<i>b</i> (Å)	11.6210(5)	20.3859(8)	15.834(2)
	<i>c</i> (Å)	14.7202(7)	7.6875(4)	20.513(3)
	α (°)	80.474(4)	90	90
	β (°)	76.222(4)	90	95.960(10)
	γ (°)	87.184(4)	90	90
	Ζ	4	4	4
	V (Å ³)	1673.92(14)	1929.17(16)	1898.6(5)
	d_x (g/cm ³)	1.36	1.14	1.28
	F(000)	712	712	776
	$\mu \ (\mathrm{mm}^{-1})$	0.39	0.51	0.73
	θ range (°)	2.9-25.0	2.2-75.3	3.5-75.7
	Reflections			
	Collected	28095	7463	7974
	Unique (R_{int})	5895 (0.039)	3363 (0.028)	3818 (0.022)
	With $I > 2\sigma(I)$	3891	2817	3379
	$R(F)[I > 2\sigma(I)]$	0.0515	0.0639	0.0372
	w $R(F^2)$ $[I > 2\sigma(I)]$	0.1011	0.1762	0.0898
	R(F) (all data)	0.0896	0.0731	0.0425
	w $R(F^2)$ (all data)	0.1163	0.1873	0.0943
	Goodness of fit	1.03	1.06	1.05
	Max/min $\Delta \rho$ (e/Å ³)	0.18/-0.21	0.42/-0.20	0.21/-0.19

Conclusion

In summary, a mild route for the synthesis of α , α' -bis(substituted-benzylidene)cycloalkanones is reported under green conditions. Operational simplicity, simple workup without column chromatographic purification, reusability of the catalyst, tolerance of various functional groups, and high yields of products are the main advantages of this protocol. Moreover, five new products and three new single crystals are reported.

Experimental

Chemicals were purchased from the Merck and Aldrich chemical companies. Thinlayer chromatography (TLC) on commercial aluminum-backed plates of silica gel 60 F254 was used to monitor the progress of reactions. The products were characterized by FT-IR spectra, ¹H NMR, ¹³C NMR. FT-IR spectra were recorded on a Shimadzu FT-IR-8400 instrument. ¹H and ¹³C NMR spectra were recorded on a Bruker Advance Spectrometer 300 and 75 MHz, respectively, using $CDCl_3$ -d as the solvent. The chemical shifts are expressed in parts per million (ppm) and tetramethylsilane (TMS) was used as an internal reference. Melting points were recorded on a THERMO SCIENTIFIC 9100 apparatus.

Diffraction data were collected by the ω -scan technique on an Agilent Technologies diffractometer [33] for compounds 3r and 3x at 130(1) K on a SuperNova system with an Atlas CCD detector, equipped with a Nova microfocus Cu-K α radiation source ($\lambda = 1.54178$ Å), while for the compound **3n**, an Xcalibur with an Eos CCD detector and graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) was used. The data were corrected for Lorentz polarization as well as for absorption effects [33]. Precise unit-cell parameters were determined by a least-squares fit of 4554 (3n), 2919 (3r), and 5222 (3x) reflections of the highest intensity, chosen from the whole experiment. The structures were solved with SIR-92 [34] and refined by the full-matrix method with SHELX-2013 [35]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in 3r were positioned geometrically and refined as riding on appropriate carrier atom; their displacement parameters were set at 1.2 or 1.5 (CH₃) times U_{eq} of the carrier atoms. All hydrogen atoms in **3n** and **3x** were located in the difference Fourier maps and freely refined. In the structure of 3r, the central ring has been found as disordered over two positions with 0.793(16)/0.207(16) occupancies; geometry of the less-occupied fragment was constrained. Relevant crystal data are listed in Table 3 together with refinement details.

CCDC 1030225 (**3n**), 1030226 (**3r**), and 1030227 (**3x**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

X-ray powder diffraction analyses were conducted using a Bruker D8 X-ray diffractometer (Cu-K α radiation, k = 1.54) for characterization of the heterogeneous catalyst. Transmission electron microscopy (TEM) was carried out with a Philips CM10 instrument. TGA were conducted on a Du Pont 2000 thermal analysis apparatus under air atmosphere at a heating rate of 5 °C/min.

Preparation of nano-TiO₂

Nano-TiO₂ was prepared by the hydrothermal method. $NH_3 \cdot H_2O$ was added to TiCl₄ solution until the pH value was 1.8. After stirring for 2 h at 70 °C, the final pH of the solution was adjusted to 6. The resulting suspension was aged at ambient temperature for 24 h. The final product was filtered, washed with NH_4Ac -HOAc until no Cl⁻ was detected. Then the precipitate was separated using a centrifuge, was washed with ethanol, and dried in a vacuum. After 2 h treatment at 650 °C, TiO₂ nanoparticles were obtained [29].

General procedure for the synthesis of α , α' -bis(substitutedbenzylidene)cycloalkanone derivatives

A mixture of aldehyde (2 mmol), cycloalkanone (1 mmol), 20 mol% of nano-TiO₂ (0.016 g), and 20 drops of glacial acetic acid was refluxed in ethanol (5 mL) for an appropriate time. After completion of the reaction (monitored by TLC), the catalyst was filtered. Yellowish crystals of the products were obtained by slow evaporation of an ethanol solution under room temperature.

Spectral data of some selected compounds

α , α' -bis(2-nitrobenzylidene)cyclopentanone (**3d**)

Yellow crystal; M.P. 168–171 °C; IR (KBr, cm⁻¹): v_{max} : 3080, 2914, 1691, 1517, 1473; ¹H NMR (300 MHz, CDCl₃): δ 2.88 (s, 4H), 7.52–7.86 (m, 8H, ArH), 8.10 (s, 2H); ¹³CNMR (75 MHz, CDCl₃): δ 25.98, 125.03, 129.57, 129.66, 130.59, 131.18, 133.11, 140.14, 148.86, 194.33.

α , α' -bis(4-cyanobenzylidene)cyclohexanone (**3**q)

Yellow crystal; M.P. 207–211 °C; IR (KBr, cm⁻¹): v_{max} : 2223, 1666, 1577, 1500, 1139; ¹H NMR (300 MHz, CDCl₃): δ 1.83 (m, 2H), 2.91 (m, 4H), 7.52–7.71 (m, 8H, ArH), 7.75 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 22.56, 28.30, 112.00, 118.51, 130.57, 132.14, 135.18, 135.22, 138.23, 140.20, 189.29.

 α , α' -bis-benzylidene-4-(tert-butyl)cyclohexanone (**3r**)

Yellow crystal; M.P. 137–140 °C; IR (KBr, cm⁻¹): v_{max} : 3083, 2867, 1660, 1490, 1446; ¹H NMR (300 MHz, CDCl₃): δ 0.96 (m, 9H), 1.5 (m, 1H), 2.47 (m, 2H), 3.18 (m, 2H),7.33–7.49 (m, 10H, ArH), 7.78 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 27.27, 29.51, 32.56, 44.42, 128.45, 128.53, 130.30, 136.04, 136.16, 136.85, 190.64.

 α , α' -bis(2-nitrobenzylidene)-4-(tert-butyl)cyclohexanone (**3s**)

Yellow crystal; M.P. 209–212 °C; IR (KBr, cm⁻¹): ν_{max} : 3075, 2960, 1674, 1519, 1440; ¹H NMR (300 MHz, CDCl₃): δ 0.78 (s, 9H), 1.50 (m, 1H), 2.18(m, 2H), 2.75(m, 2H), 7.37–8.15 (m, 8H, ArH), 8.17 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 26.92, 29.02, 32.59, 44.24, 125.00, 129.08, 130.94, 132.05, 133.22, 136.04, 137.28, 148.19, 188.82.

 α , α' -bis(2-chlorobenzylidene)-4-(tert-butyl)cyclohexanone (**3***t*)

Yellow crystal; M.P. 181–183 °C; IR (KBr) (cm⁻¹) v_{max} : 3026, 2960, 2864, 1668, 1467, 1434; ¹H NMR (300 MHz, CDCl₃): δ 0.86 (s, 9H), 1.51 (tt, *J* = 12.62 Hz, 3.1 Hz, 1H), 2.32 (m, 2H), 2.97 (dd, *J* = 15.3 Hz/2.2 Hz, 2H), 7.26–7.46 (m, 8H,

ArH), 7.90 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 27.11, 29.36, 32.60, 44.43, 126.34, 129.56, 129.80, 130.27, 134.04, 134.37, 134.95, 137.68, 189.88.

α , α' -bis(4-flurobenzylidene)-4-(tert-butyl)cyclohexanone (3x)

Yellow crystal; M.P. 174–177 °C; IR (KBr) (cm⁻¹) v_{max} : 2956, 2869, 1664, 1602, 1508, 1155; ¹H NMR (300 MHz, CDCl₃): δ 0.95 (s, 9H), 1.47 (tt, J = 12.7/2.8 Hz, 1H), 2.41 (m, 2H), 3.11 (dd, J = 15.6/2.3 Hz, 2H), 7.08–7.47 (m, 8H, ArH), 7.73 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 27.23, 29.37, 32.49, 44.32, 115.45, 115.73, 132.02, 132.06, 132.11, 132.22, 135.65, 135.68, 135.78, 160.94, 164.26, 190.22.

 α , α' -bis(4-bromobenzylidene)-4-(tert-butyl)cyclohexanone (**3y**)

Yellow crystal; M.P. 161–164 °C; IR (KBr) (cm⁻¹) v_{max} : 2958, 2867, 1662, 1604, 1487, 1074; ¹H NMR (300 MHz, CDCl₃): δ 0.94 (s, 9H), 1.47 (tt, J = 12.8/3.2 Hz, 1H), 2.40 (m, 2H), 3.09 (dd, J = 15.5/2.3 Hz, 2H), 7.30–7.56 (m, 8H, ArH), 7.68 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 27.22, 29.42, 32.51, 44.26, 122.89, 131.71, 134.73, 135.76, 136.48, 190.06.

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