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Efficient Method for the Synthesis of α,α' -Bis(arylmethylidene) Cycloalkanones Catalyzed by Bromodimethylsulfonium Bromide

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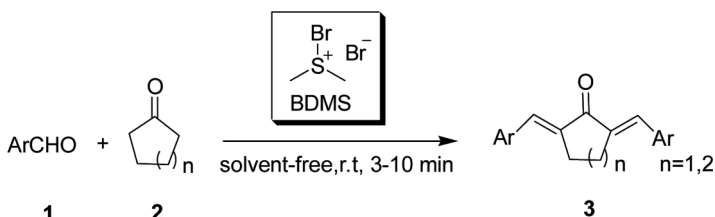
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EFFICIENT METHOD FOR THE SYNTHESIS OF α,α' -BIS(ARYLMETHYLIDENE) CYCLOALKANONES CATALYZED BY BROMODIMETHYLSULFONIUM BROMIDE

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GRAPHICAL ABSTRACT



Abstract Bromodimethylsulfonium bromide (BDMS)-catalyzed crossed aldol condensation between aromatic aldehydes and ketones is reported to access α,α' -bis(arylmethylidene) cycloalkanones at room temperature in good yields within 3–10 min. The salient features of this method are the simplicity of the procedure, the ready accessibility of the catalyst, and greater yields in relatively short reaction times.

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications[®] for the following free supplemental resource(s): Full experimental and spectral details.]

Keywords α,α' -Bis(arylmethylidene) cycloalkanones; bromodimethylsulfonium bromide (BDMS); crossed aldol condensation; solvent-free

INTRODUCTION

The α,α' -bis(arylmethylidene) cycloalkanones are very important precursors to potentially bioactive pyrimidine derivatives;^[1] intermediates of agrochemical, perfumes, and pharmaceuticals;^[2] new organic material for nonlinear optical applications;^[3] cytotoxic analogs;^[4] and the units of liquid-crystalline polymers.^[5] The crossed-aldol

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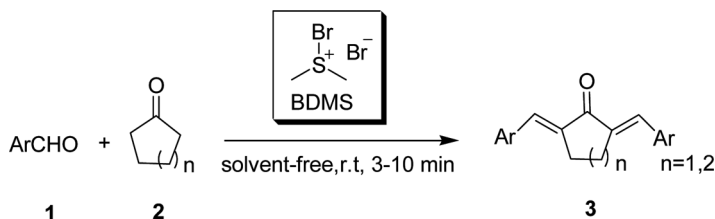
condensation reaction is suitable for these preparations and can be carried out using strong acid or base catalysts.^[6]

Different complexes of metal (II) ions have also been used as catalysts for this cross reaction but the yields (<38%) were not satisfactory.^[7] Improved approaches have been reported for the synthesis of α,α' -bis(arylmethylidene) cycloalkanones including KF-supported reagents,^[8,9] Yb(OTf)₃,^[10] iodotrimethylsilane,^[11] TiCl₃(SO₃CF₃),^[12] RuCl₃,^[13] Pd/C-Me₃SiCl,^[14] SOCl₂,^[15] SmI₃,^[16] LiOH,^[17] KOH,^[18,19] TMSCl,^[20] LiClO₄-TMSNEt₂,^[21] 2,4,6-trichloro-1,3,5-triazine (TCT),^[22] FeCl₃,^[23] Cp₂TiPh₂,^[24] bis(p-ethoxyphenyl)telluroxide,^[25] Cp₂ZrH₂,^[26] BF₃·OEt₂,^[27] InCl₃,^[28] and animal bone meal (ABM)^[29] as catalysts or activators. A good yield of the corresponding products, however, can be obtained only at elevated temperature, and the purification operations are always complicated. The cross-aldol reaction has also been operated at room temperature using I₂ as catalyst but the reaction time is long.^[30] Thus, the development of new catalytic methods is highly desirable.

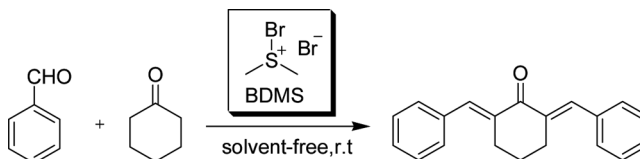
Bromodimethylsulfonium bromide (BDMS) is a readily accessible, cheap, and highly effective reagent^[31] as well as a catalyst for various organic transformations.^[32] Recently, Yadav et al. reported the efficiency of BDMS in Beckmann rearrangement (BKR).^[33] In addition, very recently they have demonstrated the virtue of this catalyst for multicomponent synthesis of 3-aminoalkylated indoles.^[34] In continuation of our work on the development of new synthetic methodologies,^[35] we sought to explore the advantages of this reagent further for other important transformations. Here we report an efficient, convenient, and facile method for the condensation of aldehydes with cycloalkanones leading to the corresponding α,α' -bis(arylmethylidene) cycloalkanones in the presence of BDMS as a catalyst Scheme 1.

RESULTS AND DISCUSSION

The condensation reaction of benzaldehyde (2 mmol) with cyclohexanone (1 mmol) was carried out at room temperature. In the study of catalyst loading, 0, 1, 5, 10, and 15 mol% of BDMS were tested. Reactions with both 10% and 15% catalysts both gave quantitative yields in 4 min (Table 1, entries 4 and 5), while the reaction with 5 mol% loading only gave 85% yield even after a long reaction time of 25 min. In the absence of catalyst, the reaction did not yield any product at room temperature even after a long reaction time. This result suggests that BDMS plays a critical role in this reaction.



Scheme 1. Crossed-aldol condensation catalyzed by BDMS.

Table 1. BDMS-catalyzed reactions of benzaldehyde with cyclohexanone^a

Entry	BDMS (mol%)	Time (min)	Yield ^b (%)
1	0	120	0
2	1	40	76
3	5	25	85
4	10	4	98
5	15	4	98

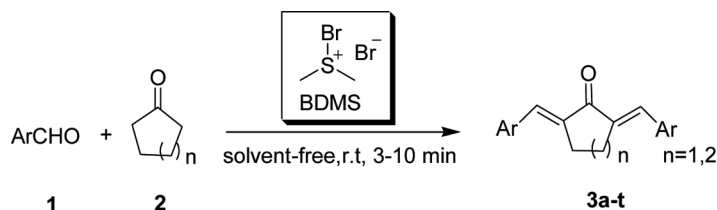
^aRoom temperature.^bIsolated yield.

To demonstrate the generality and scope of this method, various aromatic aldehydes such as 4-nitrobenzaldehyde, 4-methoxybenzaldehyde, and 4-chlorobenzaldehyde were treated with cycloalkanones in the presence of catalytic amounts of BDMS (10 mol%) under solvent-free conditions, and the obtained results are summarized in Table 2. All the yields were excellent, including the heteroaromatic aldehydes such as 2-furaldehyde and 2-thiophenecarboxaldehyde. Aromatic aldehydes containing both electron-donating (Me, MeO, OH) and electron-withdrawing (NO₂, Cl) groups underwent the conversion smoothly. Both cyclopentanone and cyclohexanone showed similar activity toward the condensation with aromatic aldehydes. All the reactions were free from by-products usually found in classical reaction conditions.^[6] The purification of these compounds was easily performed by simple filtration and recrystallization with alcohol.

The *EE* geometry of the double bonds in these compounds (**3a–t**) was based on earlier literature reports.^[36–38] It is reported that the vinylic protons are in close proximity to the carbonyl group, which exerted an anisotropic effect, resulting in the downfield shifting and overlapping of the vinylic protons with the aromatic protons and the appearance of vinylic protons in the region of δ 7.15–7.95 ppm is an indication of such compounds with *E*-configuration and in the region of δ 6.8 ppm indicates *Z*-configuration.^[36,37] For example, the olefinic protons of *Z*-2-phenyl methylenecyclohexanones and *Z*-2-phenyl methylene-6,6-diphenyl cyclohexanones are generally observed at δ 6.27 and 6.22 ppm.^[38]

We used BDMS as a source of HBr to catalyze this reaction and found it to be an excellent catalyst for preparation of α,α' -bis(arylmethylidene) cycloalkanones. A plausible mechanism is shown in Scheme 2. Accordingly, BDMS (10 mol%) reacts with the aromatic aldehyde and releases 2 mol of HBr and 1 mol of DMSO (removable by washing with water) as the by-products. The in situ-generated HBr acts as a protic acid and activates the carbonyl oxygen to promote the condensation to give the products.

Some critical mechanistic information for the reaction of benzaldehyde with cyclopentanone was collected by experimental investigations (Scheme 3). The benzaldehyde could efficiently react with cyclopentanone with the aid of HBr (20 mol%) as catalyst,

Table 2. Preparation of α,α' -bis(arylmethylidene) cycloalkanones catalyzed by BDMS at room temperature under solvent-free conditions^a

Entry	n	Ar	Product	Time (min)	Yield (%) ^b	Mp (°C) (lit.) ^[ref]
1	1	Ph	3a	3	96	191–192 (188–190) ^[10]
2	1	4-OCH ₃ C ₆ H ₄	3b	3	94	210–212 (211–212) ^[10]
3	1	4-CH ₃ C ₆ H ₄	3c	4	93	240–242 (243–244) ^[10]
4	1	4-ClC ₆ H ₄	3d	8	93	230–231 (228–229) ^[10]
5	1	2,4-Cl ₂ C ₆ H ₃	3e	5	95	204–205 (206–207) ^[10]
6	1	4-NO ₂ C ₆ H ₄	3f	10	85	231–233 (229–231) ^[10]
7	1	3-pyridyl	3g	8	88	220–222 (222–224) ^[10]
8	1	4-OHC ₆ H ₄	3h	10	85	>300 (>300) ^[10]
9	1	C ₆ H ₄ CH=CH	3i	5	93	217–219 (215–216) ^[10]
10	1	2-furyl	3j	4	92	166–168 (163–164) ^[10]
11	2	Ph	3k	4	98	115–117 (117–118) ^[10]
12	2	4-OCH ₃ C ₆ H ₄	3l	4	95	163–165 (161–163) ^[10]
13	2	4-CH ₃ C ₆ H ₄	3m	4	93	161–162 (164–165) ^[10]
14	2	4-ClC ₆ H ₄	3n	3	95	147–148 (147–148) ^[13]
15	2	2,4-Cl ₂ C ₆ H ₃	3o	8	90	162–164 (163–164) ^[10]
16	2	4-NO ₂ C ₆ H ₄	3p	10	85	162–163 (161–162) ^[10]
17	2	4-N(CH ₃) ₂ C ₆ H ₄	3q	10	85	251–253 (250–252) ^[10]
18	2	4-OHC ₆ H ₄	3r	10	87	294–296 (290–292) ^[10]
19	2	C ₆ H ₄ CH=CH	3s	5	93	178–179 (177–178) ^[10]
20	2	2-Thienyl	3t	4	94	140–142 (142–143) ^[10]

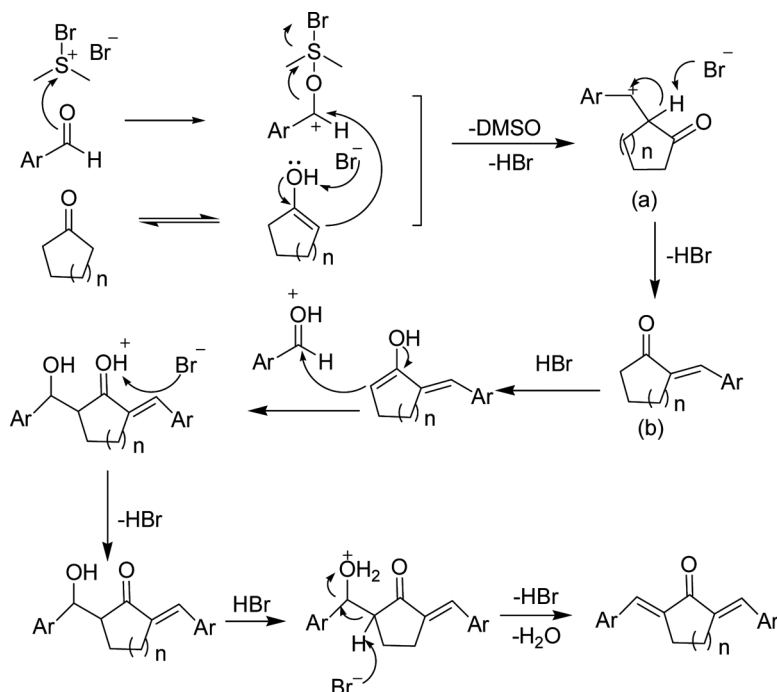
^aRoom temperature.^bIsolated yield.

giving the corresponding product **3a** in 95% yield. This result suggests that HBr plays the critical role in this reaction.

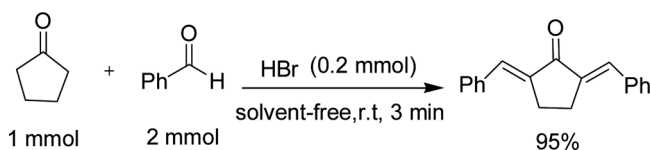
In comparison with other catalysts such as Yb(OTf)₃, Cp₂TiPh₂, RuCl₃, I₂, ABM, Na/animal bone meal (Na/ABM), and TCT, which were recently used in the synthesis of α,α' -bis(arylmethylidene) cycloalkanones, BDMS employed here exhibits more effective catalytic activity than those previously reported in terms of the reaction temperature, yields, and reaction time (Table 3). All the products obtained were fully characterized by infrared (IR), ¹H NMR, ¹³C NMR, and elemental analyses. The spectral data were also compared with the reported values.

EXPERIMENTAL

All chemicals were purchased from Aldrich Co. and used as received. Melting points were measured using a X-4 apparatus and are uncorrected. IR spectra were obtained using Shimadzu FTIR-8900 spectrometer instrument. NMR spectra were



Scheme 2. Plausible mechanistic illustration of BDMS-catalyzed crossed-aldol condensation reaction.



Scheme 3. Crossed-aldol condensation of benzaldehyde with cyclopentanone catalyzed by HBr.

taken with a Varian 400 spectrometer. Elemental analyses were carried out on MT-3 analyzer. Physical and spectral characterization of the products was confirmed by comparison with available literature data.^[10,13]

Table 3. Comparison of the effect of catalysts for the synthesis of product **3k**

Catalyst/solvent	Temperature (°C)	Time	Yield (%)	Ref.
Yb(OTf) ₃	90	6 h	94	10
Cp ₂ TiPh ₂	120	6 h	73	25
RuCl ₃	120	6 h	95	13
I ₂	rt	4.5 h	92	31
Animal bone meal (ABM)	100	1.25 h	76	30
Na/animal bone meal (Na/ABM)	100	20 min	96	30
TCT	90	20 min	90	23
BDMS	rt	4 min	98	—

General Procedure for the Synthesis of α,α' -Bis(Arylmethylidene) Cycloalkanone Derivatives

A mixture of aromatic aldehyde (2.0 mmol), cycloalkanone (1.0 mmol), and bromodimethylsulfonium bromide (0.1 mmol) was stirred at room temperature for an appropriate time (Table 2). After completion of the reaction as indicated by thin-layer chromatography (TLC), the mixture was diluted with water (10 mL), which precipitated the solid product. The product obtained was pure as found by TLC and ^1H and ^{13}C NMR spectroscopy. However, the products were further purified by recrystallization from ethanol.

α,α' -Bis(Benzylidene) Cyclohexanone 3k

IR (KBr): 3024, 2926, 1657, 1609, 1570, 1440, 1268, 1144, 773 cm^{-1} . ^1H NMR (CDCl_3): δ = 7.81 (s, 2H), 7.33–7.48 (m, 10H), 2.96 (t, J = 6.4 Hz, 4H), 1.83–1.76 (m, 2H). ^{13}C NMR (CDCl_3): δ = 187.2, 144.3, 141.5, 134.7, 128.6, 127.5, 27.8. Anal. calcd. for $\text{C}_{20}\text{H}_{18}\text{O}$: C, 87.56; H, 6.61; Found: C, 87.61; H, 6.74.

CONCLUSION

In conclusion, we have developed an expeditious, novel, and efficient method for the synthesis of α,α' -bis(arylmethylidene) cycloalkanones from aromatic aldehydes with ketones using a catalytic amount of bromodimethylsulfonium bromide at room temperature. The advantages of the current protocol include experimentally operational ease, mild reaction conditions, ready accessibility of the catalyst, and high efficiency, all of which make it a useful and attractive strategy for the preparation of various α,α' -bis(arylmethylidene) cycloalkanone derivatives simply by changing different substrates.

SUPPORTING INFORMATION

Full experimental detail and ^1H and ^{13}C NMR data can be found via the Supplementary Content section of this article's Web page.

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