Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Molecular Catalysis A: Chemical 212 (2004) 91–98
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Copper-catalyzed cyclopropanation of 1,2,3,4-tetrahydropyridin-2-ones with diazoacetates A facile and stereoselective synthesis of 3-oxo-2-azabicyclo [4.1.0] heptanes

Suman L. Jain, Bir Sain*

Chemical and Biosciences Division, Indian Institute of Petroleum, Dehradun 248005, India

Received 3 August 2003; accepted 5 November 2003

Abstract

The reactions of a series of 1,2,3,4-tetrahydropyridin-2-ones (**1**) with diazoacetates (**2**) in the presence of copper-bronze catalyst yielded exclusively 3-oxo-2-azabicyclo [4.1.0] heptanes (**3** and **4**) in excellent yields with high *exo*-selectivity. Tetrahydropyridin-2-ones (**1**) with *N*-alkyl substituents were found to be more reactive than *N*-aryl substitutents. Among the various copper catalysts studied, copper(II) triflate was found to be the best catalyst while rhodium chloride, ruthenium chloride did not catalyze the reaction. The application of ultrasonic radiation enhanced the reaction rate and allowed the reactions to be conducted at room temperature.

Keywords: Cycloaddition; Copper; Catalysis; Diazocompounds; Heterocycles

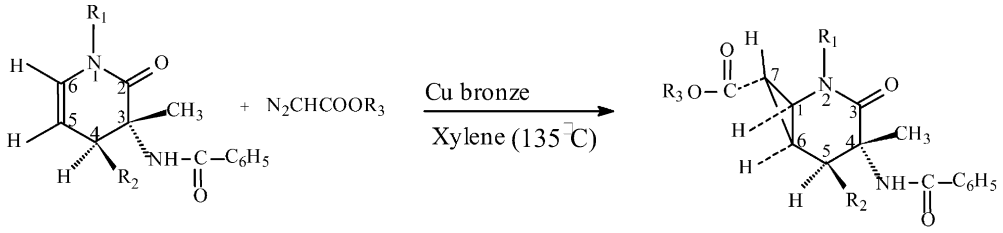
1. Introduction

The development of new transition metal catalysts and design of effective strategies for their applications have brought a renaissance in the synthetic uses of diazocarbonyl compounds for carbenoid transformations [1–3]. This has resulted in the development of efficient procedures for cyclopropanation, dipolar addition, insertion and ylide formation, both in intermolecular [4–6] and intramolecular [7,8] modes. Diazoacetates are the most important diazocarbonyl compounds and their reactions with a variety of olefins have been extensively studied [9,10] and used for the synthesis of natural and bioactive molecules [11–13]. In the recent years, while increasing emphasis is being given on the stereoselectivity [14–17] in the reactions of metal carbenoids using diazoacetates, there are also few reports, which address the chemoselectivity in the metal carbenoid reactions [18–21]. Enamines [22], an important class of olefins are known to undergo a variety of reactions, however, there are scanty and conflicting reports on their reactions with diazoacetates. In this context, Wenkert and Broquet [23] and Wang et al. [24] reported cyclopropanation of enamine double bond with ethyldiazoacetate using copper-based catalysts. In contrast, Augusti et al. [25] reported that the reaction of carbethoxycarbene produced by cupric acetylacetonate-catalyzed decomposition of ethyldiazoacetate with several acyclic enaminones, yields only the products derived from C–H insertion.

During our investigations on 1-aza-1,3-butadienes, we encountered a new and fairly general reaction which provides facile synthesis of a variety of 1,2,3,4-tetrahydropyridin-2-ones (**1**) which are typical enamides [26,27]. Since pyridin-2-one ring is an important feature of many naturally occurring alkaloids and biologically active substances [28,29], and there are conflicting reports on the reactions of diazoacetates with enamines, we thought it worthwhile to study the reactions of 1,2,3,4-tetrahydropyridin-2-ones (**1**) with diazoacetates (**2**) for synthesizing novel heterocycles. Accordingly, we herein report that 1,2,3,4-tetrahydropyridin-2-ones (**1**) reacted with diazoacetates (**2**) in presence of catalytic amount of copper-bronze to yield 3-oxo-2-azabicyclo [4.1.0] heptanes (**3** and **4**) with high *exo*-selectivity and without any evidence for the formation

* Corresponding author. Tel.: +91-135-660071; fax: +91-135-660202.
E-mail address: birsain@iip.res.in (B. Sain).

1381-1169/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2003.11.008



1 **2** **3**

3	R_1	R_2	R_3
a	CH_3	C_6H_5	C_2H_5
b	$CH_2(CH_2)_2CH_3$	C_6H_5	C_2H_5
c	CH_3	C_6H_5	CH_3
d	$CH_2(CH_2)_2CH_3$	C_6H_5	CH_3
e	C_6H_{11}	C_6H_5	C_2H_5
f	C_6H_{11}	C_6H_5	CH_3
g	$C_6H_4CH_3$(p)	C_6H_5	C_2H_5
h	$C_6H_4CH_3$(p)	C_6H_5	CH_3
i	$CH_2CH_2CH_3$	C_6H_5	C_2H_5
j	$CH_2CH_2CH_3$	C_6H_5	CH_3
k	C_6H_{11}	CH_3	C_2H_5
l	C_6H_{11}	CH_3	CH_3
m	$C_6H_4OCH_3$ (p)	C_6H_5	C_2H_5
n	C_6H_5	C_6H_5	CH_3

4 **5** **6**

Scheme 1.

of products which could arise from allylic C–H insertion (**5**) or product formed by cyclopropanation and insertion (**6**) (Scheme 1).

2. Results and discussion

3-Benzoylamino-1,3-dimethyl-4-phenyl-1,2,3,4-tetrahydropyridin-2-one (**1**, $R_1 = CH_3$, $R_2 = C_6H_5$) when reacted with excess of ethyldiazoacetate (**2**, $R_3 = C_2H_5$) in presence of catalytic amount of freshly activated copper-bronze in refluxing xylene for 6 h, yielded the separation of a white crystalline solid which was filtered on a Buckner funnel and recrystallized from benzene, mp 264–65 °C, yield 75%. The structural assignment 4-benzoylamino-7-*exo*-ethoxycarbonyl-2,4-dimethyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**3a**) to this product rests on elemental as well as spectral analyses. The FAB mass spectra showed ($M^+ + 1$) at *m*/*z* 407. The 300 MHz ^{1}H NMR spectra of **3a** taken in $CDCl_3$ showed signals at δ: 1.26 (t, 3H, $J = 7.1$ Hz, $COOCH_2C\mathbf{H}_3$), 1.48 (s, 3H, CH_3), 2.09 (dd, 1H, $J = 2.7, 4.5$ Hz, H-7), 2.39 (ddd, 1H, $J = 4.5, 7.2, 8.7$ Hz, H-6), 3.14 (s, 3H, N–CH_3), 3.23 (dd, 1H, $J = 2.7, 8.7$ Hz, H-1), 4.12 (q, 2H, $J = 7.1$ Hz, $COOC\mathbf{H}_2CH_3$), 4.35 (d, 1H, $J = 7.2$ Hz, H-5), 5.68 (broad s, 1H, NH), 7.23–7.48 (m, 8H, Ar H), 7.62 (m, 2H, Ar H). The values of the coupling constants for H-1, H-6 and H-7 were determined by recording homonuclear spin–spin decoupled ^{1}H NMR spectra. The ^{13}C NMR (100 MHz, $CDCl_3$) of **3a** (δ): 13.5 ($COOCH_2\mathbf{C}H_3$), 18.5 (CH_3), 23.8 (CH-7), 32.1 (CH-6), 33.1 (N–CH_3), 40.6 (CH-5), 44.3 (CH-1), 59.1 (C-4), 60.3 ($COO\mathbf{C}H_2CH_3$), 126.8–130.6 (Ar C), 167.4 (CO,

NH–C=O), 170.3 (CO, −3), 171.3 (CO, **C**OOCH$_2$CH$_3$). The ^{13}C NMR assignments were confirmed by recording fully decoupled distortionless enhancement by polarization transfer (DEPT) spectra. The IR spectrum (KBr) showed bands at 3330, 1709 and 1681 cm^{-1} indicating the presence of NH, ester and amido carbonyl groups, respectively. The possible formation of 1,2,3,4-tetrahydropyridin-2-one (**5**) and 3-oxo-2-azabicyclo [4.1.0] heptane (**6**) were eliminated on the basis of mass and NMR spectra. The filtrate obtained after removal of the **3a** from the reaction mixture was evaporated under vacuum and separated on TLC (SiO_2) to yield 4-benzoylamino-7-*endo*-ethoxycarbonyl-2,4-dimethyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**4a**) as white crystalline solid, mp 253–54 °C, yield 8%. The structural assignment **4a** rests on elemental as well as spectral analysis. The FAB mass spectra showed ($M^+ + 1$) at *m*/*z* 407. The 300 MHz ^{1}H NMR spectra of **4a** in $CDCl_3$ showed peaks at δ: 1.25 (t, 3H, J = 7.1 Hz, COOCH$_2$C**H**$_3$), 1.46 (s, 3H, CH$_3$), 1.89 (dd, 1H, J = 6.5, 7.9 Hz, H-7), 2.26 (ddd, 1H, J = 6.3, 7.7, 7.9 Hz, H-6), 3.04 (s, 3H, N–CH$_3$), 3.21 (dd, 1H, J = 6.3, 6.5 Hz, H-1), 4.26 (q, 2H, J = 7.1 Hz, COOC**H**$_2$CH$_3$), 4.92 (d, 1H, J = 7.7 Hz, H-5), 6.01 (broad s, 1H, NH), 7.26–7.46 (m, 8H, Ar H), 7.62 (m, 2H, Ar H). The values of the coupling constants for H-1, H-6 and H-7 were determined by recording homonuclear spin–spin decoupled ^{1}H NMR spectra. The IR spectrum (KBr) showed bands at 3325, 1721 and 1680 cm^{-1} indicating the presence of NH, ester and amido carbonyl groups, respectively. The stereochemistry of cyclopropyl esters (*exo*/*endo*) were assigned by ^{1}H NMR spectroscopy wherein the *endo*-isomer showed upfiled value for H-7 relative to the *exo*-isomer. The obtained values of the coupling constants for the H-7 ($^3J_{7,1}$ = 2.7 Hz, $^3J_{7,6}$ = 4.5 Hz for *exo*-isomer and $^3J_{7,1}$ = 6.5 Hz, $^3J_{7,6}$ = 7.9 Hz for *endo*-isomer) also support the *exo* and *endo* assignments of 3-oxo-2-azabicyclo [4.1.0] heptane (**3** and **4**).

Similarly 3-benzoylamino-1-*n*-butyl-3-methyl-4-phenyl-1,2,3,4-tetrahydropyridin-2-one (**1**, R$_1$ = *n*−butyl, R$_2$ = C$_6$H$_5$) when reacted with excess of ethyldiazoacetate (**2**, R$_3$ = C$_2$H$_5$) yielded 4-benzoylamino-2-*n*-butyl-7-*exo*-ethoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**3b**) as white crystalline solid, mp 172–73 °C in 70% yield and 4-benzoylamino-2-*n*-butyl-7-*endo*-ethoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**4b**) as viscous oil in 10% yield. The 300 MHz ^{1}H NMR spectra of **3b** in $CDCl_3$ showed signals at δ: 0. 99 (m, 3H, N–CH$_2$CH$_2$CH$_2$C**H**$_3$), 1.25 (t, 3H, J = 7.1 Hz, COOCH$_2$C**H**$_3$), 1.45 (s, 3H, CH$_3$), 1.66–1.68 (m, 4H, N–CH$_2$C**H**$_2$C**H**$_2$CH$_3$), 2.07 (dd, 1H, J = 4.5, 4.8 Hz, H-7), 2.38 (ddd, J = 4.8, 7.5, 9.0 Hz, 1H, H-6), 3.23 (dd, 1H, J = 4.5, 9.0 Hz, H-1), 3.51 (m, 2H, N–C**H**$_2$CH$_2$CH$_2$CH$_3$), 4.13 (q, 2H, J = 7.1 Hz, COOC**H**$_2$CH$_3$), 4.35 (d, 1H, J = 7.5 Hz, H-5), 5.75 (broad s, 1H, NH), 7.22–7.50 (m, 8H, Ar H), 7.65 (m, 2H, Ar H). IR spectrum (KBr) showed bands at 3325, 1710 and 1680 cm^{-1} indicating the presence of NH, ester and amido carbonyl groups, respectively. The FAB mass spectra showed ($M^+ + 1$) at *m*/*z* 449. The 300 MHz ^{1}H NMR spectra of **4b** in $CDCl_3$ showed signals at δ: 0.99 (m, 3H, N–CH$_2$CH$_2$CH$_2$C**H**$_3$), 1.24 (t, 3H, J = 7.1 Hz, COOCH$_2$C**H**$_3$), 1.45 (s, 3H, CH$_3$), 1.66–1.68 (m, 4H, N–CH$_2$C**H**$_2$C**H**$_2$CH$_3$), 1.90 (dd, 1H, J = 6.3, 8.7 Hz, H-7), 2.85 (ddd, 1H, J = 7.2, 7.5, 8.7 Hz, H-6), 3.31 (dd, 1H, J = 6.3, 7.2 Hz, H-1), 3.51 (m, 2H, N–C**H**$_2$CH$_2$CH$_2$CH$_3$), 4.13 (q, 2H, J = 7.1 Hz, COOC**H**$_2$CH$_3$), 4.93 (d, 1H, J = 7.5 Hz, H-5), 6.10 (broad s, 1H, NH), 7.23–7.48 (m, 8H, Ar H), 7.65 (m, 2H, Ar H). The stereochemical assignments (*exo*/*endo*) were again based on the relative value of H-7 in ^{1}H NMR spectra and supported by the obtained values of coupling constants for H-7 ($^3J_{7,1}$ = 4.5 Hz, $^3J_{7,6}$ = 4.8 Hz for *exo*-isomer and $^3J_{7,1}$ = 6.3 Hz, $^3J_{7,6}$ = 8.7 Hz for *endo*-isomer). The IR spectrum (KBr) showed bands at 3328, 1728 and 1685 cm^{-1} indicating the presence of NH, ester and amido carbonyl groups, respectively. FAB mass spectra showed ($M^+ + 1$) at *m*/*z* 449.

The relative stereochemistry of 1,2,3,4-tetrahydropyridin-2 one (**1**, R$_1$ = CH$_3$, R$_2$ = C$_6$H$_5$) was established by recording difference NOE spectra. Irradiation of the proton H-4 δ 5.20 showed NOE at the C$_6$H$_5$ δ 7.20 which is geminal to it and did not show NOE at the CH$_3$ signal δ 1.42 which is vicinal to it, similarly irradiation at CH$_3$ signal δ 1.42 showed NOE at NH δ 5.83 which is geminal to it, at C$_6$H$_5$ δ 7.20 which is in *cis*-position and no NOE was observed at H-4 δ 5.20,confirming that H-4 and CH$_3$ are in *trans*-position. The difference NOE spectra were also recorded with 3-oxo-2-azabicyclo [4.1.0] heptane (**3a**) and it was observed that relative stereochemistry of substituents at C-4 and C-5 remain same as in the (**1**, R$_1$ = CH$_3$, R$_2$ = C$_6$H$_5$). Similarly the relative stereochemistry of the groups attached at C-4, and C-5 in 3-oxo-2-azabicyclo [4.1.0] heptane (**4a**) was confirmed by recording difference NOE spectra and was found essentially to be the same as in **3a**.

The reaction was generalized by reacting a series of 1,2,3,4-tetrahydropyridin-2-ones (**1**) with ethyldiazoacetates and methyldiazoacetates (Scheme 1). The reaction was found to be highly chemoselective, stereoselective and yielded exclusively 3-oxo-2-azabicyclo [4.1.0] heptanes (**3** and **4**) with high *exo*-selectivity in excellent yields, without any evidence for the formation of insertion products like **5** or **6**. 1,2,3,4-Tetrahydropyridin-2-ones with *N*-alkyl substituents were found to be more reactive than *N*-aryl substituents. To evaluate the effect of various catalysts in these reactions, the reaction of 3-benzoylamino-1,3-dimethyl-4-phenyl-1,2,3,4-tetrahydropyridin-2-one (**1**, R$_1$ = CH$_3$, R$_2$ = C$_6$H$_5$) with ethyldiazoacetate (**2**, R$_3$ = C$_2$H$_5$) was conducted in presence of different catalysts (Table 1). As shown in results, copper-based catalysts in general were found to be good, while rhodium chloride and ruthenium chloride probably being better catalysts for C–H insertion reactions [5,6] showed lack of reactivity in these reactions. Among the various copper-based catalysts, copper(II) triflate was found to be most promising for these transformations.

Table 1
Effect of various catalysts

Compound	Diazoester	Catalyst	Reaction time (h)	Yield of **3a** (%)
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	Copper bronze	6	75
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	$CuSO_4$	8	65
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	$Cu(acac)_2$	4	75
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	Cu(II) triflate[a]	2.5	80
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	$RuCl_3{\cdot}XH_2$ O	12	–
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	$RhCl_3{\cdot}XH_2$ O	12	–

Substrate (1 mmol), catalyst (0.1 mmol), xylene (15 ml, refluxing), EDA (5 mmol).
[a] Experiment was run in dichloromethane at room temperature under N_2 blanket.

Table 2
Effect of various solvents

Compound	Diazoester	Solvent	Reaction time (h)	Yield of **3a** (%)
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	Xylene	6	75
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	Benzene	6	40
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	Dichloromethane	12	20
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	Chlorobenzene	8	65
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	Dimethylformamide	15	–

Substrate (1 mmol), catalyst (0.1 mmol), solvent (15 ml, refluxing) and EDA (5 mmol).

Reaction of 3-benzoylamino-1,3-dimethyl-4-phenyl-1,2,3,4-tetrahydropyridin-2-one (**1**, $R_1 = CH_3$, $R_2 = C_6H_5$) with ethyldiazoacetate in presence of catalytic amounts of copper-bronze was studied in different solvents with a view to evaluate the effect of solvent in these reactions. These results are presented in Table 2. Among the solvents studied, xylene was found to be good solvent for this reaction. However, with the use of Cu(II) triflate as catalyst, the reaction could be efficiently carried out at room temperature in dichloromethane. Although a series of tetrahydropyridin-2-ones (**1**) reacted efficiently with both ethyldiazoacetate and methyldiazoacetate, however, there was no reaction with ethyldiazomalonate.

Ultrasonic radiation have been found to be very effective in promoting various types of reactions and are finding increasing applications in synthetic organic transformations [30,31]. Reaction of 3-benzoylamino-1,3-dimethyl-4-phenyl-1,2,3,4-tetrahydropyridin-2-one (**1**, $R_1 = CH_3$, $R_2 = C_6H_5$) with ethyldiazoacetate (**2**) in presence of copper catalysts were carried out under sonochemical conditions. To the best of our knowledge, there is no literature report on the effect of ultrasonic radiation in the reactions of diazoesters. The results obtained in these experiments are summarized in Table 3. Surprisingly, the use of ultrasonic radiation not only promote the rate of these reactions but also provides a new and effective methodology where the reaction of ethyldiazoacetate with tetrahydropyridin-2-one (**1**) in presence of catalysts Cu-bronze, $CuSO_4$, $Cu(acac)_2$ catalysts could be carried out at room temperature. It is worth mentioning that without the use of ultrasonic radiation these reactions could be carried out at room temperature only by using Cu(II) triflate as catalyst. Further investigations on the use of ultrasonic radiation in the reactions of diazoacetates are being carried out.

In summary, 1,2,3,4-tetrahydropyridin-2-ones, typical enamides undergo highly chemoselective and stereoselective reaction with carbenes generated from copper-catalyzed decomposition of diazoacetates to yield corresponding 3-oxo-2-aza-bicyclo [4.1.0] heptanes in excellent yields with high *exo*-selectivity without any evidence for the formation of product which could arise from C–H insertion or product formed by cyclopropanation and insertion.

Table 3
Effect of ultrasonic radiation

Compound	Diazoester	Catalyst	Reaction time (h)	Yield of **3a** (%)
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	Copper bronze	5	70
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	$CuSO_4$	2.5	70
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	$Cu(acac)_2$	1.5	75
1 ($R_1 = CH_3$, $R_2 = C_6H_5$)	EDA	Cu(II) triflate[a]	1	78

Substrate (1 mmol), catalyst (0.1 mmol), xylene (15 ml), EDA (5 mmol), room temperature.
[a] Experiment was run in dichloromethane at room temperature under N_2 blanket.

3. Experimental

3.1. Materials

1,2,3,4-Tetrahydropyridin-2-one (**1**) were prepared by reacting 1-aza-1,3-butadienes with 4-methyl-2-phenyl-2-oxazolin-5-one. [32]. Ethyldiazoacetate and methyldiazoacetate were prepared by conventional literature method [33]. Diethyldiazomelonate was prepared following the procedure reported by Regitz et al. [34] and Ando et al. [35]. Copper-bronze was prepared by reported procedure [36,37]. Copper(II) acetylacetonate, Copper(II) triflate, rhodium chloride and ruthenium chloride used were commercially available.

3.2. Reaction of 1,2,3,4-tetrahydropyridin-2-ones (1) with diazoacetates (2): typical procedure

To the stirred and refluxing solution of 3-benzoylamino-1,3-dimethyl-4-phenyl-1,2,3,4-tetrahydropyridin-2-one (**1**, $R_1 = CH_3$, $R_2 = C_6H_5$, 320 mg, 1 mmol), containing freshly activated copper-bronze (63 mg, 0.1 mmol, 10 mol%) in dry xylene (15 ml), the solution of ethyldiazoacetate (570 mg, 5 mmol) in dry xylene (5 ml) was drop wise added over a period of 0.5 h. The stirring was further continued with refluxing for a period of 6 h till the reaction was completed (TLC, SiO_2, ethyl acetate:benzene 1:4). The reaction mixture was then stored overnight at room temperature. The separated solid was filtered on a Buckner funnel and recrystallized from benzene to yield 4-benzoylamino-7-*exo*-ethoxycarbonyl-2,4-dimethyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**3a**) as white crystalline solid, mp 264–65 °C, yield 305 mg (75%). The filtrate obtained after separating the white crystalline solid from the reaction mixture was evaporated under vacuum and separated on TLC (SiO_2) using ethyl acetate, benzene (1:4) as eluent to yield 4-benzoylamino-7-*endo*-ethoxycarbonyl-2,4-dimethyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**4a**) as white crystalline solid, mp 253–54 °C, yield 32 mg (8%). Similarly 3-benzoylamino-1-*n*-butyl-3-methyl-4-phenyl-1,2,3,4-tetrahydropyridin-2-one (**1**, $R_1 = n-$butyl, $R_2 = C_6H_5$) when reacted with ethyldiazoacetate yielded 4-benzoylamino-2-*n*-butyl-7-*exo*-ethoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**3b**) as white crystalline solid, mp 172–173 °C, in 70% yield and 4-benzoylamino-2-*n*-butyl-7-*endo*-ethoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane(**4b**) as viscous oil in 10% yield. The 3-oxo-2-azabicyclo [4.1.0] heptanes (**3c**–**3n**) were similarly prepared and their corresponding *endo*-isomers (**4c**–**4n**) were not isolated. The 3-oxo-2-azabicyclo [4.1.0] heptanes (**3c**–**3f** and **3i**–**3l**) did not separate as solid from reaction mixture these compounds were isolated by TLC (SiO_2). For carrying out experiments under sonochemical conditions the sonicator probe was dipped slightly in the reaction mixture containing 1,2,3,4-tetrahydropyridin-2-one (1 mmol), ethyldiazoacetate (5 mmol), catalyst (0.1 mmol) in xylene (15 ml) and the ultrasonic radiation were applied at room temperature.

3.3. Product identification

Melting points were determined in open capillary tubes on a Büchi apparatus and are uncorrected. The ^{1}H NMR spectra were recorded on Bruker 300 MHz and 400 MHz spectrometers and chemical shift values are recorded in δ units (ppm) relative to Me_4Si as internal standard. The ^{13}C NMR (100 MHz) spectra were recorded on Bruker 400 MHz instrument with proton noise decoupling and chemical shift values are expressed in δ values relative to Me_4Si as internal standard. The distortionless enhancement by polarization transfer spectra were recorded at $\Theta = \pi/2$, $3\pi/4$ and $\pi/4$ to assign the ^{13}C values of CH_3, CH_2, CH and quaternary carbons. Homonuclear spin–spin decoupled ^{1}H NMR spectra were recorded by using DIGMOD homodecoupling digital pulse program. IR spectra were recorded on a Perkin-Elmer 1760X FTIR spectrometer in potassium bromide disc or neat thin film. Mass spectra were recorded on matrix assisted laser desorption ionization (MALDI) mass spectrometer. Soniprep-150 with exponential microprobe was used for carrying out experiments in sonochemical conditions.

3.3.1. 4-Benzoylamino-7-exo-ethoxycarbonyl-2,4-dimethyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (3a)

Reaction time 6 h; white crystalline solid; 75%; mp 264–65 °C. IR (KBr): 3330, 1709, 1681 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 1.26 (t, 3H, $J = 7.1$ Hz, $COOCH_2C\mathbf{H}_3$), 1.48 (s, 3H, CH_3), 2.09 (dd, 1H, $J = 2.7$, 4.5 Hz, H-7), 2.39 (ddd, 1H, $J = 4.5$, 7.2, 8.7 Hz, H-6), 3.14 (s, 3H, N–CH_3), 3.23 (dd, 1H, $J = 2.7$, 8.7 Hz, H-1), 4.12 (q, 2H, $J = 7.1$ Hz, $COOC\mathbf{H}_2CH_3$), 4.35 (d, 1H, $J = 7.2$ Hz, H-5), 5.68 (broad, s, 1H, NH), 7.23–7.48 (m, 8H, Ar H), 7.62 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 13.5 ($COOCH_2\mathbf{C}H_3$), 18.5 (CH_3), 23.8 (CH-7), 32.1 (CH-6) 33.1 (N–CH_3), 40.6 (CH-5), 44.3 (CH-1), 59.1 (C-4), 60.3 ($COO\mathbf{C}H_2CH_3$), 126.8–130.6 (Ar C), 167.4 (CO, NH–C=O), 170.3 (CO, −3), 171.3 (CO, $\mathbf{C}OOCH_2CH_3$). Mass *m*/*z* 407 ($M^+ + 1$). Anal. calcd. for $C_{24}H_{26}N_2O_4$: C, 70.91; H, 6.16; N, 7.14. Found: C, 70.61; H, 6.40; N, 6.85.

3.3.2. 4-Benzoylamino-7-endo-ethoxycarbonyl-2,4-dimethyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (4a)

Reaction time 6 h; white crystalline solid; 8%; mp 253–54 °C. IR (KBr): 3325, 1721, 1680 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 1.25 (t, 3H, $J = 7.1$ Hz, $COOCH_2C\mathbf{H}_3$), 1.46 (s, 3H, CH_3), 1.89 (dd, 1H, $J = 6.5$, 7.9 Hz, H-7), 2.26 (ddd, 1H, $J = 6.3$, 7.7, 7.9 Hz, H-6), 3.04 (s, 3H, N–CH_3), 3.21 (dd, 1H, $J = 6.3$, 6.5 Hz, H-1), 4.26 (q, 2H, $J = 7.1$ Hz, $COOC\mathbf{H}_2CH_3$), 4.92 (d, 1H, $J = 7.7$ Hz, H-5), 6.01 (broad s, 1H, NH), 7.26–7.46 (m, 8H, Ar H), 7.62 (m, 2H, Ar H). Mass *m*/*z* 407 ($M^+ + 1$). Anal. calcd. for $C_{24}H_{26}N_2O_4$: C, 70.91; H, 6.16; N, 7.14. Found: C, 70.52; H, 6.29; N, 7.02.

*3.3.3. 4-Benzoylamino-2-n-butyl-7-exo-ethoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**3b**)*

Reaction time 5 h; white crystalline solid; 70%; mp 172–73 °C. IR (KBr): 3325, 1710, 1680 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 0.99 (m, 3H, N–$CH_2CH_2CH_2CH_3$), 1.25 (t, 3H, J = 7.1 Hz, $COOCH_2CH_3$), 1.45 (s, 3H, CH_3), 1.66–1.68 (m, 4H, N–$CH_2CH_2CH_2CH_3$), 2.07 (dd, 1H, J = 4.5, 4.8 Hz, H-7), 2.38 (ddd, J = 4.8, 7.5, 9.0 Hz, 1H, H-6), 3.23 (dd, 1H, J = 4.5, 9.0 Hz, H-1), 3.51 (m, 2H, N–$CH_2CH_2CH_2CH_3$), 4.13 (q, 2H, J = 7.1 Hz, $COOCH_2CH_3$), 4.35 (d, 1H, J = 7.5 Hz, H-5), 5.75 (broad s, 1H, NH), 7.22–7.50 (m, 8H, Ar H), 7.65 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 13.7 ($COOCH_2CH_3$), 14.1 (N–$CH_2CH_2CH_2CH_3$), 19.5 (CH_3), 20.0 (N–$CH_2CH_2CH_2CH_3$), 23.7 (CH-7), 29.3 (N–$CH_2CH_2CH_2CH_3$), 33.3 (CH-6), 39.5 (CH-5), 44.8 (CH-1), 46.5 (N–$CH_2CH_2CH_2CH_3$), 59.6 (C-4), 60.9 ($COOCH_2CH_3$), 126.9–138.0 (Ar C), 167.7 (CO, NH–C=O), 170.5 (CO, −3), 171.3 (CO, $COOCH_2CH_3$). Mass *m/z* 449 ($M^+ + 1$). Anal. calcd. for $C_{27}H_{32}N_2O_4$: C, 72.29; H, 7.19; N, 6.25. Found: C, 72.32; H, 7.18; N, 6.29.

*3.3.4. 4-Benzoylamino-2-n-butyl-7-endo-ethoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**4b**)*

Reaction time 5 h; 10%; viscous oil. IR (thin film): 3328, 1728, 1685 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 0.99 (m, 3H, N–$CH_2CH_2CH_2CH_3$), 1.24 (t, 3H, J = 7.1 Hz, $COOCH_2CH_3$), 1.45 (s, 3H, CH_3), 1.66–1.68 (m, 4H, N–$CH_2CH_2CH_2CH_3$), 1.90 (dd, 1H, J = 6.3, 8.7 Hz, H-7), 2.85 (ddd, 1H, J = 7.2, 7.5, 8.7 Hz, H-6), 3.31 (dd, 1H, J = 6.3, 7.2 Hz, H-1), 3.51 (m, 2H, N–$CH_2CH_2CH_2CH_3$), 4.13 (q, 2H, J = 7.1 Hz, $COOCH_2CH_3$), 4.93 (d, 1H, J = 7.5 Hz, H-5), 6.10 (broad s, 1H, NH), 7.23–7.48 (m, 8H, Ar H), 7.65 (m, 2H, Ar H). Mass *m/z* 449 ($M^+ + 1$). Anal. calcd. for $C_{27}H_{32}N_2O_4$: C, 72.29; H, 7.19; N, 6.25. Found: C, 72.49; H, 7.27; N, 6.52.

*3.3.5. 4-Benzoylamino-7-exo-methoxycarbonyl-2,4-dimethyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**3c**)*

Reaction time 8 h; white crystalline solid; 70%; mp 250–51 °C. IR (KBr): 3349, 1714 1681 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 1.48 (s, 3H, CH_3), 2.11 (dd, 1H, J = 2.7, 3.5 Hz, H-7), 2.39 (ddd, 1H, J = 3.5, 7.2, 8.7 Hz, H-6), 3.14 (s, 3H, N–CH_3), 3.20 (dd, 1H, J = 2.7, 8.7 Hz, H-1), 3.67 (s, 3H, $COOCH_3$), 4.34 (d, 1H, J = 7.2 Hz, H-5), 5.69 (broad s, 1H, NH), 7.23–7.47 (m, 8H, Ar H), 7.63 (m, 2H, Ar H). Mass *m/z* 393 ($M^+ + 1$). Anal. calcd. for $C_{23}H_{24}N_2O_4$: C, 72.39; H, 6.16; N, 7.14. Found: C, 72.41; H, 6.14; N, 7.16.

*3.3.6. 4-Benzoylamino-2-n-butyl-7-exo-methoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**3d**)*

Reaction time 8 h; white crystalline solid; 80%; mp 170–71 °C. IR (KBr): 3340, 1715 1685 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 0.98 (m, 3H, N–$CH_2CH_2CH_2CH_3$), 1.45 (s, 3H, CH_3), 1.66–1.68 (m, 4H, N–$CH_2CH_2CH_2CH_3$), 2.10 (dd, 1H, J = 4.2, 4.5 Hz, H-7), 2.39 (ddd, 1H, J = 4.5, 7.5, 8.2 Hz, H-6), 3.23 (dd, 1H, J = 4.2, 8.2 Hz, H-1), 3.51 (m, 2H, N–$CH_2CH_2CH_2CH_3$), 3.67 (s, 3H, $COOCH_3$), 4.34 (d, 1H, J = 7.5 Hz, H-5), 5.68 (broad s, 1H, NH), 7.23–7.48 (m, 8H, Ar H), 7.67 (m, 2H, Ar H); *m/z* 435 ($M^+ + 1$). Anal. calcd. for $C_{26}H_{30}N_2O_4$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.85; H, 6.90; N, 6.38.

*3.3.7. 4-Benzoylamino-2-cyclohexyl-7-exo-ethoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**3e**)*

Reaction time 6 h; white crystalline solid; 70%; mp 260–261 °C. IR (KBr): 3350, 1710, 1682 cm^{-1}. ^1H NMR ($CDCl_3$, δ) 1.26 (t, 3H, J = 7.1 Hz, $COOCH_2CH_3$), 1.40–2.10 (m, 14H, CH_3, H-7, cyclohexyl H), 2.37 (ddd, 1H, J = 4.5, 7.5, 8.5 Hz, H-6), 3.16 (dd, 1H, J = 2.5, 8.5 Hz, H-1), 4.10 (q, 2H, J = 7.1 Hz, $COOCH_2CH_3$), 4.28 (d, 1H, J = 7.5 Hz, H-5), 4.48 (m, 1H, N–CH of cyclohexyl), 5.67 (broad s, 1H, NH), 7.22–7.50 (m, 8H, Ar H), 7.66 (m, 2H, Ar H). Mass *m/z* 475 ($M^+ + 1$). Anal. calcd. for $C_{29}H_{34}N_2O_4$: C, 73.39; H, 7.22; N, 5.90. Found: C, 73.41; H, 7.19; N, 5.85.

*3.3.8. 4-Benzoylamino-2-cyclohexyl-7-exo-methoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**3f**)*

Reaction time 10 h; white crystalline solid; 65%, mp 234–35 °C. IR (KBr): 3350, 1712, 1685 cm^{-1}. ^1H NMR ($CDCl_3$, δ) 1.28–2.10 (m, 14H, CH_3, H-7, cyclohexyl H), 2.36 (ddd, 1H, J = 4.2, 7.2, 8.7 Hz, H-6), 3.16 (dd, 1H, J = 2.8, 8.7 Hz, H-1), 3.69 (s, 3H, $COOCH_3$), 4.28 (d, 1H, J = 7.2 Hz, H-5), 4.48 (m, 1H, N–CH of cyclohexyl), 5.68 (broad s, 1H, NH), 7.23–7.48 (m, 8H, Ar H), 7.67 (m, 2H, Ar H). Mass *m/z* 461 ($M^+ + 1$). Anal. calcd. for $C_{28}H_{32}N_2O_4$: C, 73.02; H, 7.00; N, 6.08. Found: C, 73.05; H, 7.02; N, 6.05.

*3.3.9. 4-Benzoylamino-7-exo-ethoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-p-tolyl-2-azabicyclo [4.1.0] heptane (**3g**)*

Reaction time 8 h; white crystalline solid; 55%; mp 254–55 °C. IR (KBr): 3360, 1714, 1690 cm^{-1}. ^1H NMR ($CDCl_3$, δ) 1.25 (t, 3H, J = 7.1 Hz, $COOCH_2CH_3$), 1.44 (s, 3H, CH_3), 2.10 (dd, 1H, J = 3.1, 4.3 Hz, H-7), 2.35 (s, 3H, $C_6H_5CH_3$), 2.39 (ddd, 1H, J = 4.3, 7.2, 8.5 Hz, H-6), 3.26 (dd, 1H, J = 3.1, 8.5 Hz, H-1), 4.12 (q, 2H, J = 7.1 Hz, $COOCH_2CH_3$), 4.41 (d, 1H, J = 7.2 Hz, H-5), 5.85 (broad s, 1H, NH), 7.20–7.49 (m, 12H, Ar H), 7.62 (m, 2H, Ar H). Mass *m/z* 483 ($M^+ + 1$). Anal. calcd. for $C_{30}H_{30}N_2O_4$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.62; H, 6.29; N, 5.71.

*3.3.10. 4-Benzoylamino-7-exo-methoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-p-tolyl-2-azabicyclo [4.1.0] heptane (**3h**)*

Reaction time 8 h; white crystalline solid; 70%; mp 240–241 °C. IR (KBr): 3355, 1718, 1690 cm^{-1}. ^1H NMR ($CDCl_3$, δ) 1.42 (s, 3H, CH_3), 2.11 (dd, 1H, J = 2.9, 4.5 Hz, H-7), 2.35 (s, 3H, $C_6H_5CH_3$), 2.39 (ddd, 1H, J = 4.5, 7.2, 8.5 Hz, H-6), 3.25 (dd, 1H, J = 2.9, 8.5 Hz, H-1), 3.68 (s,

3H, $COOCH_3$), 4.41 (d, 1H, $J = 7.2$ Hz, H-5), 5.90 (broad s, 1H, NH), 7.20–7.50 (m, 12H, Ar H), 7.64 (m, 2H, Ar H). Mass *m/z* 469 ($M^+ + 1$). Anal. calcd. for $C_{29}H_{28}N_2O_4$: C, 74.34; H, 6.02; N, 5.98. Found: C, 74.31; H, 6.04; N, 5.82.

*3.3.11. 4-Benzoylamino-7-exo-ethoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-n-propyl-2-azabicyclo [4.1.0] heptane (**3i**)*

Reaction time 5 h; white crystalline solid; 70%; mp 210–211 °C. IR (KBr): 3340, 1708, 1680 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 1.01 (m, 3H, N–$CH_2CH_2C\mathbf{H}_3$), 1.25 (t, 3H, $J = 7.1$ Hz, $COOCH_2C\mathbf{H}_3$), 1.48 (s, 3H, CH_3), 1.72 (m, 2H, N–$CH_2C\mathbf{H}_2CH_3$), 2.09 (dd, 1H, $J = 2.7$, 3.5 Hz, H-7), 2.40 (ddd, 1H, $J = 3.5$, 7.4, 8.5 Hz, H-6), 3.24 (dd, 1H, $J = 2.7$, 8.5 Hz, H-1), 3.50 (m, 2H, N–$C\mathbf{H}_2CH_2CH_3$), 4.14 (q, 2H, $J = 7.1$ Hz, $COOC\mathbf{H}_2CH_3$), 4.35 (d, 1H, $J = 7.4$ Hz, H-5) 5.80 (broad s, 1H, NH), 7.22–7.50 (m, 8H, Ar H), 7.64 (m, 2H, Ar H). Mass *m/z* 435 ($M^+ + 1$). Anal. calcd. for $C_{26}H_{30}N_2O_4$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.91; H, 6.85; N, 6.40.

*3.3.12. 4-Benzoylamino-7-exo-methoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-n-propyl-2-azabicyclo [4.1.0] heptane (**3j**)*

Reaction time 6 h; white crystalline solid; 75%; mp 215–216 °C. IR (KBr): 3340, 1714, 1685 cm^{-1}. ^1H NMR ($CDCl_3$, δ) 1.01 (m, 3H, N–$CH_2CH_2C\mathbf{H}_3$), 1.45 (s, 3H, CH_3), 1.71 (m, 2H, N–$CH_2C\mathbf{H}_2CH_3$), 2.10 (dd, 1H, $J = 2.7$, 3.4 Hz, H-7), 2.40 (ddd, 1H, $J = 3.4$, 7.4, 8.5 Hz, H-6), 3.24 (dd, 1H, $J = 2.7$, 8.5 Hz, H-1) 3.51 (m, 2H, N–$C\mathbf{H}_2CH_2CH_3$), 3.68 (s, 3H, $COOCH_3$), 4.35 (d, 1H, $J = 7.4$ Hz, H-5), 5.68 (broad s, 1H, NH), 7.23–7.50 (m, 8H, Ar H), 7.65 (m, 2H, Ar H). Mass *m/z* 421 ($M^+ + 1$). Anal. calcd. for $C_{25}H_{28}N_2O_4$: C, 71.41; H, 6.71; N, 6.66 Found: C, 71.17; H, 6.82; N, 6.68.

*3.3.13. 4-Benzoylamino-2-cyclohexyl-7-exo-ethoxycarbonyl-4,5-dimethyl-3-oxo-2-azabicyclo [4.1.0] heptane (**3k**)*

Reaction time 4 h; white crystalline solid; 80%; mp 156–57 °C. IR (KBr): 3335, 1710, 1685 cm^{-1}. ^1H NMR ($CDCl_3$, δ) 1.01 (d, 3H, CH_3), 1.25 (t, 3H, $J = 7.1$ Hz, $COOCH_2C\mathbf{H}_3$), 1.38–2.10 (m, 14H, CH_3, H-7, cyclohexyl H), 2.30 (m, 1H, H-6), 3.12 (dd, 1H, $J = 2.7$, 8.5 Hz, H-1) 3.45 (m, 1H, H-5), 4.11 (q, 2H, $J = 7.1$ Hz, $COOC\mathbf{H}_2CH_3$), 4.44 (m, 1H, N–CH of cyclohexyl), 6.29 (broad s, 1H, NH), 7.25–7.48 (m, 3H, Ar H), 7.68 (m, 2H, Ar H). Mass *m/z* 413 ($M^+ + 1$). Anal. calcd. for $C_{24}H_{32}N_2O_4$: C, 69.88; H, 7.82; N, 6.79. Found: C, 69.81; H, 7.85; N, 6.88.

*3.3.14. 4-Benzoylamino-2-cyclohexyl-7-exo-methoxycarbonyl-4,5-dimethyl-3-oxo-2-azabicyclo [4.1.0] heptane (**3l**)*

Reaction time 4 h; white crystalline solid; 70%; mp 140–141 °C. IR (KBr): 3330, 1718, 1680 cm^{-1}. ^1H NMR ($CDCl_3$, δ) 1.09 (d, 3H, CH_3), 1.28–2.10 (m, 14H, CH_3, H-7, cyclohexyl H), 2.30 (m, 1H, H-6), 3.13 (dd, 1H, $J = 2.8$, 8.4 Hz, H-1) 3.45 (m, 1H, H-5), 3.70 (s, 3H, $COOCH_3$), 4.45 (m, 1H, NCH of cyclohexyl), 5.90 (broad s, 1H, NH), 7.25–7.48 (m, 3H, Ar H), 7.70 (m, 2H, Ar H). Mass *m/z* 399 ($M^+ + 1$). Anal. calcd. for $C_{23}H_{30}N_2O_4$: C, 69.32; H, 7.59; N, 7.03. Found: C, 69.81; H, 7.62; N, 7.15.

*3.3.15. 2-p-Anisoyl-4-benzoylamino-7-exo-ethoxycarbonyl-4-methyl-3-oxo-5-phenyl-2-azabicyclo [4.1.0] heptane (**3m**)*

Reaction time 12 h; white crystalline solid; 50%; mp 285–86 °C. IR (KBr): 3315, 1709, 1690 cm^{-1}. ^1H NMR ($CDCl_3$, δ) 1.23 (t, 3H, $J = 7.1$ Hz, $COOCH_2C\mathbf{H}_3$), 1.38 (s, 3H, CH_3), 2.11 (dd, 1H, $J = 2.7$, 3.5 Hz, H-7), 2.40 (ddd, 1H, $J = 3.5$, 7.2, 8.5 Hz, H-6), 3.51 (dd, 1H, $J = 2.7$, 8.5 Hz, H-1), 3.81 (s, 3H, OCH_3), 4.15 (q, 2H, $J = 7.1$ Hz, $COOC\mathbf{H}_2CH_3$), 4.45 (d, 1H, $J = 7.2$ Hz, H-5), 5.90 (broad s, 1H, NH), 7.20–7.50 (m, 12 H, Ar H), 7.67 (m, 2H, Ar H). Mass *m/z* 499 ($M^+ + 1$). Anal. calcd. for $C_{30}H_{30}N_2O_5$: C, 72.27; H, 6.06; N, 5.62. Found: C, 72.48; H, 6.18; N, 5.70.

*3.3.16. 4-Benzoylamino-7-exo-methoxycarbonyl-4-methyl-3-oxo-2,5-diphenyl-2-azabicyclo [4.1.0] heptane (**3n**)*

Reaction time 12 h; white crystalline solid; 40%; mp 280–81 °C. IR (KBr): 3325, 1708, 1685 cm^{-1}. ^1H NMR ($CDCl_3$, δ) 1.37 (s, 3H, CH_3), 2.11 (dd, 1H, $J = 2.7$, 3.2 Hz, H-7), 2.42 (ddd, 1H, $J = 3.2$, 7.2, 8.5 Hz, H-6), 3.53 (dd, 1H, $J = 2.7$, 8.5 Hz, H-1), 3.68 (s, 3H, $COOCH_3$), 4.46 (d, 1H, $J = 7.2$ Hz, H-5), 5.98 (broad s, 1H, NH), 7.20–7.50 (m, 13H, Ar H), 7.68 (m, 2H, Ar H). Mass *m/z* 455 ($M^+ + 1$). Anal. calcd. for $C_{28}H_{26}N_2O_4$: C, 73.99; H, 5.76; N, 6.16. Found: C, 73.78; H, 5.70; N, 6.28.

Acknowledgements

Authors are thankful to RSIC (Lucknow) for recording ^1H NMR, ^{13}C NMR spectra, for carrying out the DEPT, NOE, homonuclear spin–spin decoupled experiments and IICT, Hyderabad for recording mass spectra. We are thankful to Analytical Sciences Division of this laboratory for recording IR, NMR spectra and other analyses. One of us (SLJ) thanks CSIR, New Delhi for award of Senior Research Fellowship.

References

[1] M.P. Doyle, M.A. Mckervey, J. Chem. Soc., Chem. Commun. (1997) 983.
[2] M.P. Doyle, D.C. Forbes, Chem. Rev. 98 (1998) 911.
[3] A. Padwa, S.F. Hornbuckle, Chem. Rev. 91 (1991) 203.
[4] M.P. Doyle, M.A. Mckervey, T. Ye, Modern Catalytic Methods for Organic Synthesis with Diazocompounds, Wiley, New York, 1997.
[5] P. Muller, S. Tohill, Tetrahedron 56 (2000) 1725.
[6] M.P. Doyle, I.M. Phillips, Tetrahedron Lett. 42 (2001) 3155.
[7] M.P. Doyle, A.B. Dyatkin, G.H.P. Roos, F. Canas, D.A. Pierson, A. Van Basten, P. Muller, P. Polleux, J. Am. Chem. Soc. 116 (1994) 4507.

[8] M.P. Doyle, A.V. Kaliin, D.G. Ene, J. Am. Chem. Soc. 118 (1996) 8837.
[9] M.P. Doyle, Chem. Rev. 86 (1986) 919.
[10] M.P. Doyle, D.C. Forbes, Chem. Rev. 98 (1998) 911.
[11] J. Salauin, Chem. Rev. 89 (1989) 1247.
[12] M.P. Doyle, Chem. Rev. 86 (1986) 919.
[13] M.P. Doyle, Recl. Trav. Chim. Pay-Bas. 110 (1991) 305.
[14] M. Brookhart, W.B. Studabaker, Chem. Rev. 87 (1987) 411.
[15] E. Galardon, P.L. Maux, G. Simonneaux, Tetrahedron 56 (2000) 615.
[16] M.P. Doyle, R.E. Austin, A.S. Bailey, M.P. Dwyer, A.B. Dyatkin, A.V. Kalinin, M.M.Y. Kwan, S. Liras, C.J. Oalmann, R.J. Pieters, M.N. Protopopova, C.E. Raab, G.H.P. Roos, Q.L. Zhou, S.F. Martin, J. Am. Chem. Soc. 117 (1995) 5763.
[17] Z. Li, Z. Zheng, B. Wan, H. Chen, J. Mol. Catal. A: Chem. 165 (2001) 67.
[18] H.M.L. Davies, E. Saikali, W.B. Young, J. Org. Chem. 56 (1991) 5696.
[19] S.J. Adam, R. Frenette, M. Belley, F. Chibante, J.P. Springer, J. Am. Chem. Soc. 109 (1987) 5432.
[20] S. Hashimoto, N. Watanabe, S. Ikegami, J. Chem. Soc., Chem. Commun. (1992) 1508.
[21] A. Padwa, D.J. Austin, S.F. Hornbuckle, A. Semones, M.P. Doyle, M.N. Protopopova, J. Am. Chem. Soc. 114 (1992) 1874.
[22] P.W. Hickmott, Tetrahedron 38 (1982) 1975.
[23] E. Wenkert, C. Broquet, Synth. Commun. 9 (1979) 689.
[24] M.W. Wang, M. An, B. Fang, Chin. Chem. Lett. 6 (1995) 556.
[25] R. Augusti, M.N. Eberlin, C. Kascheres, J. Heterocycl. Chem. 32 (1995) 1355.
[26] J.S. Sandhu, B. Sain, Heterocycles 26 (1987) 777.
[27] B. Sain, J.N. Baruah, J.S. Sandhu, J. Heterocycl. Chem. 19 (1982) 1511.
[28] J.S. Glasby, Encyclopedia of the Alkaloids, Plenum Press, New York, 1975.
[29] R.A. Abramovitch (Ed.), Pyridine and its Derivatives, Supplement 3, Wiley, New York, 1975.
[30] J.H. Luche Synthetic Organic Sono Chemistry, Plenum Press, New York, 1998.
[31] J. Lindley, T.J. Mason, Chem. Soc. Rev. 16 (1987) 275.
[32] J.S. Sandhu, B. Sain, Heterocycles 26 (1987) 777.
[33] E.B. Womack, A.B. Nelson, Org. Synth. Coll. 3 (1955) 392.
[34] M. Regitz, J. Hocker, A. Liedhegener, Org. Synth. Coll. 5 (1973) 179.
[35] W. Ando, S. Kondo, T. Migita, J. Am. Chem. Soc. 91 (1969) 6516.
[36] J.E. Hodgkins, R.J. Flores, J. Org. Chem. 28 (1963) 3356.
[37] R.T. La Londe, M.A. Tobias, J. Am. Chem. Soc. 86 (1964) 4068.