Heteroatom Chemistry
Volume 18, Number 1, 2007

A Highly Efficient Method for Solvent-Free Synthesis of Bisarylmethylidenes of Pyranones and Thiopyranones

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Received 25 September 2005; revised 19 December 2005

ABSTRACT: *A remarkable efficient double crossed aldol condensation of heterocyclic ketones with a variety of aromatic aldehydes is described at room temperature in the presence of magnesium bromide ethyl etherate, triethylamine, and methanol under solvent-free conditions. Excellent yields of 3,5-bisarylmethylidenes of pyranones and thiopyranones are achieved in a facile one-pot general procedure.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:44–49, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20252

INTRODUCTION

We are interested in the development of the chemistry of heterocyclic compounds [1]. Substituted derivatives of tetrahydropyran-4-one (**1**) and tetrahydrothiopyran-4-one (**2**) are useful key precursors for a vast number of heterocyclic synthetic preparations [2], and direct substitution at different positions of **1** and **2** is therefore interesting [3]. In addition, substituted products of thiopyranone **2** are attractive as well since they could be converted via removal of sulfur atom to α,β-unsaturated ketones which are not easily prepared by direct standard procedures [4]. The strategy to use such skeletons for construction of various synthetic targets is well established and has been recently demonstrated by Ward et al. for the synthesis of polypropionate building blocks [5].

Crossed aldol condensation of homocyclic ketones **3** and **4** with aldehydes [6] is a useful method for the preparation of bis(arylmethylidene)cycloalkanones which are very important synthetic precursors [7]. Many developments have been achieved in recent years to widen the synthetic scope of bisarylmethylidenes of homocyclic ketones [8] by microwave irradiation [9], ultrasound mediation [10], and Lewis acid catalysis [11]. Although similar reactions for some heterocyclic ketones are reported [12], lack of a general efficient and reliable method for the synthesis of bisarylmethylidenes of various heterocyclic ketones has been obvious until recently that we communicated a $LiClO_4$ mediated synthetic procedure for the preparation of bis(arylmethylidene)thio-pyranones [3].

In recent years, mild Lewis acidic salts [13] such as magnesium bromide diethyl etherate ($MgBr_2{\cdot}OEt_2$) [14] have been widely used for various organic transformations. Our experiences on the use of such reagents [15], prompted us to be looking for mild media for versatile synthesis of the title compounds. Treatment of alcohols with $MgBr_2{\cdot}OEt_2$ and triethylamine (TEA) is speculated to produce species equivalent to magnesium alkoxides [16], which are able to trigger the aldol condensation of ketones with

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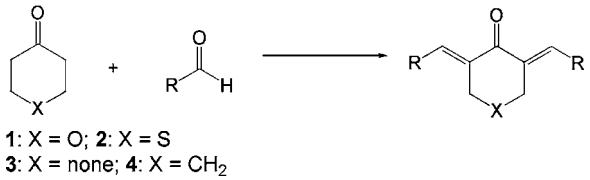
Contract grant sponsor: Ministry of Science, Research, and Technology of Iran.



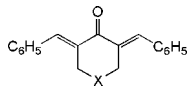
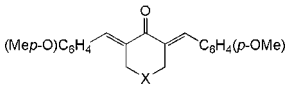
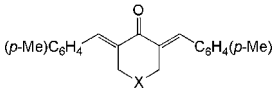
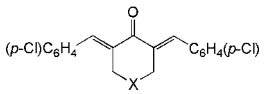
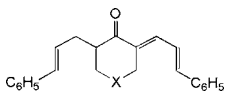
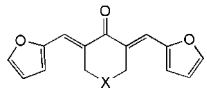
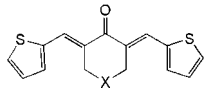
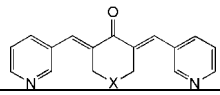
SCHEME 1

aldehydes via removal of α-hydrogen of the ketone under very mild conditions. In the present article, a 1:1:2 mixture of $MgBr_2{\cdot}OEt_2$, methanol, and TEA is employed to induce one-pot double condensation of heterocyclic ketones **1** and **2** with aromatic aldehydes under solvent-free conditions (Scheme 1). Products obtained from ketones **1** and **2** are currently being explored in our laboratory for the synthesis of more complex structures containing pyran and thiopyran subunits.

RESULTS AND DISCUSSION

Table 1 highlights the results for the condensation of various aromatic aldehydes with heterocyclic ketones **1** and **2**. Initially, benzaldehyde reaction with pyranone **1** in the presence of no solvent was examined at room temperature. We found that the best working conditions are obtained by using a 1:1:2 mixture of $MgBr_2{\cdot}OEt_2$, methanol, and TEA which can facilitate a rapid formation of **1a** in 92% yield (entry 1). Similarly, thiopyranone **2** was subjected to react with benzaldehyde under the same conditions and complete formation of **2a** was observed in

TABLE 1 Solvent-Free Condensation of **1** & **2** with Aromatic Aldehydes Using $MgBr_2.OEt_2$,TEA, and MeOH

Entry	*Aldehyde*	*Ketone*	*Product*	*X*	*Time (h)*	*Yield (%)*[a]
1	Benzaldehyde	**1**		**1a**: X = O	2	92
2	Benzaldehyde	**2**		**2a**: X = S	1.5	91
3	*p*-Anisaldehyde	**1**		**1b**: X = O	1.5	85
4	*p*-Anisaldehyde	**2**		**2b**: X = S	1	83
5	*p*-Methylbenzaldehyde	**1**		**1c**: X = O	1.5	85
6	*p*-Methylbenzaldehyde	**2**		**2c**: X = S	1	87
7	*p*-Chlorobenzaldehyde	**1**		**1d**: X = O	2.5	84
8	*p*-Chlorobenzaldehyde	**2**		**2d**: X = S	2	81
9	Cinnamaldehyde	**1**		**1e**: X = O	2.5	90
10	Cinnamaldehyde	**2**		**2e**: X = S	2	88
11	Furan-2-carbaldehyde	**1**		**1f**: X = O	2.5	93
12	Furan-2-carbaldehyde	**2**		**2f**: X = S	2	86
13	Thiophene-2-carbaldehyde	**1**		**1g**: X = O	2	83
14	Thiophene-2-carbaldehyde	**2**		**2g**: X = S	1.5	86
15	Pyridine-3-carbaldehyde	**1**		**1h**: X = O	3	86
16	Pyridine-3-carbaldehyde	**2**		**2h**: X = S	2.5	81

[a]Isolated yields.

less than 3 h (entry 2). The chemoselectivity of the reactions proved to be independent of the reactants ratios. Parallel reactions were carried out using **1** (**2**)/benzaldehyde ratios of 1:1 and 1:2. In all cases, the same product **1a** (**2a**) was formed in comparable quantities. Other control experiments were run to clarify the role of the reaction components. Test reactions conducted in the absence of methanol prolonged the reaction time, giving only few percents of the respective product after 24 h. Omission of $MgBr_2{\cdot}OEt_2$ or TEA from the reaction medium also led to nearly complete recovery of the starting materials. The generality of the method was demonstrated by the synthesis of similar products (**1b–h** and **2b–h**) obtained from the reactions of other aromatic aldehydes with heterocyclic ketones **1** and **2** under the same conditions. All reactions proceeded rapidly at room temperature, and complete conversions were observed in less than 3 h to obtain 81–93% of the respective products (entries 3–16).

The structures of the new products and the stereochemistry of the olefinic bonds were assigned by comparison of their physical and spectral data with those of known compounds (**1a–c**) [3,12d] and those of other similar structures [7b–7f,17]. TLC monitoring of the reaction and precipitation of the product during the process strongly indicated the formation of the desired compound before the aqueous work up. Based on these observations, a mechanistic pathway leading to bisarylmethylidenes can be depicted (Fig. 1).

EXPERIMENTAL

Reactions were monitored by TLC using silica gel coated plates and ethyl acetate/hexane solutions as the mobile phase. Melting points are uncorrected. UV spectra were recorded on a Perkin–Elmer Lambda 9 instrument. FT-IR spectra were recorded using KBr disks on a Bruker Vector-22 infrared spectrometer, and absorptions are reported as wave numbers (cm^{-1}). ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker AC 80 MHz instrument as $CDCl_3$ solutions, and the chemical shifts are expressed as δ units with Me_4Si as the internal standard. Mass spectra were obtained on a Finnigan Mat 8430 apparatus at ionization potential of 70 eV. Elemental analyses were performed using a CHN-O-Rapid Herazeus instrument. Compound **2** was prepared using available methods [18]. All other reagents were purchased from commercial sources and were freshly used after being purified by standard procedures.

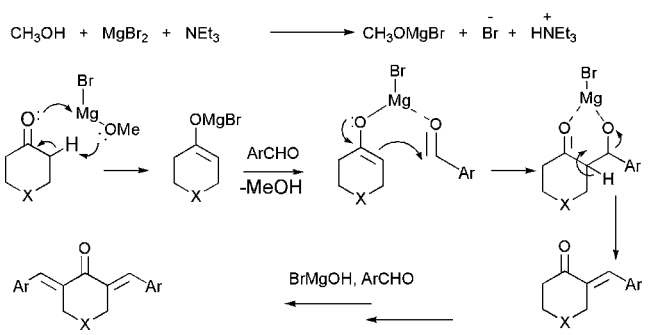


FIGURE 1 Suggested mechanistic overview of the reactions.

Bis(arylmethylidene)pyranones; Typical Procedure

Ketone **1** (1 mmol) was added to the mixture of the aldehyde (2 mmol), methanol (1 mmol), $MgBr_2{\cdot}OEt_2$ (1 mmol), and TEA (2 mmol) and the mixture was stirred at room temperature. The course of the reaction was monitored by TLC. At the end of the reaction the product precipitated out at once. Solids were washed by 0.5 M hydrochloric acid solution and then filtered. Recrystallization of the products by means of ethyl acetate yielded 83–93% of the desired compounds.

*(3E,5E)-3,5-Dibenzylidene-tetrahydropyran-4-one (***1a***).* Yellow crystals were obtained in 92% yield, mp 179–181°C (reported[12d] mp 185–187°C); UV (CH_2Cl_2, nm) λ_{max} 321; IR (KBr, cm^{-1}) 1668, 1610, 1581; ^1H NMR ($CDCl_3$) δ 4.87 (s, 4H), 7.20–7.45 (m, 10H), 7.78 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 68.6, 128.6, 129.3, 130.4, 133.2, 134.8, 136.4, 185.5; MS (70 eV) *m/z* (%) 276 ($M^{+\cdot}$, 19), 144 (22), 131 (20), 115 (100). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.19; H, 5.80.

*(3E,5E)-3,5-Bis(4-methoxybenzylidene)-tetrahydropyran-4-one (***1b***).* Yellow crystals were obtained in 85% yield, mp 170–172°C (reported [12d] mp 175–177°C); UV (CH_2Cl_2, nm) λ_{max} 361; IR (KBr, cm^{-1}) 1593, 1560, 1508; ^1H NMR ($CDCl_3$) δ 3.78 (s, 6H), 4.87 (s, 4H), 6.86 (d, 4H, $J = 8.8$ Hz), 7.23 (d, 4H, $J = 8.8$ Hz), 7.72 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 55.4, 68.6, 114.2, 127.6, 131.5, 132.4, 135.6, 160.6, 185.4; MS (70 eV) *m/z*(%) 336 ($M^{+\cdot}$, 28), 305 (5), 146 (100), 131 (69). Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.53; H, 5.96.

(3E,5E)-3,5-Bis(4-methylbenzylidene)-tetrahydropyran-4-one. (**1c**). Yellow crystals were obtained in 85% yield, mp 180–182°C (reported[12d] mp 110°C); UV (CH_2Cl_2, nm) λ_{max} 332; IR (KBr,

cm^{-1}) 1665, 1605, 1508, 1266; ^1H NMR ($CDCl_3$) δ 2.32 (s, 6H), 4.87 (s, 4H), 7.16 (s, 8 H), 7.75 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4, 68.6, 129.4, 130.7, 132.0, 132.4, 136.2, 139.7, 185.5; MS (70 eV) *m/z* (%) 304 (M^+, 26), 289 (20), 130 (63), 115 (100). Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.49; H, 6.58.

(3E,5E)-3,5-Bis(4-chlorobenzylidene)-tetrahydropyran-4-one. (**1d**). Yellow crystals were obtained in 84% yield, mp 168–170°C; UV (CH_2Cl_2, nm) λ_{max} 334; IR (KBr, cm^{-1}) 1671, 1612, 1559, 1263, 1090; ^1H NMR ($CDCl_3$): δ 4.80 (s, 4H), 7.25 (d, 4H, $J = 6.4$ Hz), 7.40 (d, 4H, $J = 6.4$ Hz), 7.70 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 68.2, 128.0, 128.8, 131.4, 133.1, 133.3, 135.0, 188.4; MS (70 eV) *m/z* (%) 344 ($M^{+\cdot}$, 22), 253 (13), 141 (82), 115 (100). Anal.Calcd for $C_{19}H_{14}Cl_2O_2$: C, 66.10; H, 4.09. Found: C, 64.93; H, 4.25.

(3E,5E)-Tetrahydro-3,5-bis((E)-3-phenylallylidene)tetrahydropyran-4-one (**1e**). Orange crystals were obtained in 90% yield, mp 206–208°C; UV (CH_2Cl_2, nm) λ_{max} 388; IR (KBr, cm^{-1}) 1734, 1660, 1587, 1216; ^1H NMR ($CDCl_3$) δ 4.77 (s, 4H), 6.80–7.80 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 67.3, 122.0, 127.4, 127.9, 128.2, 132.2, 134.8, 137.4, 142.6, 187.2; MS (70 eV) *m/z* (%): 328 ($M^{+\cdot}$, 13), 209 (12), 141 (90), 128 (48), 115 (100). Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.56; H, 6.11.

(3E,5E)-3,5-Bis((furan-2-yl)methylene)-tetrahydropyran-4-one (**1f**). Yellow crystals were obtained in 93% yield, mp 170–172°C; UV (CH_2Cl_2, nm) λ_{max} 388; IR (KBr, cm^{-1}) 1665, 1268, 756; ^1H NMR ($CDCl_3$) δ 4.97 (s, 4H), 6.45–6.57 (m, 4H), 7.35–7.52 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 68.4, 112.6, 117.4, 121.1, 130.1, 145.5, 151.8, 187.0; MS (70 eV) *m/z* (%) 256 ($M^{+\cdot}$, 18), 134 (13), 115 (9), 106 (92), 78 (100).

(3E,5E)-Tetrahydro-3,5-bis((thiophen-2-yl)methylene)pyran-4-one (**1g**). Yellow crystals were obtained in 83% yield, mp 195–197°C; UV (CH_2Cl_2, nm) λ_{max} 377; IR (KBr, cm^{-1}) 1662, 1592, 1186; ^1H NMR ($CDCl_3$): 4.90 (s, 4H), 7.00–7.50 (m, 6H), 7.87 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 68.3, 127.9, 128.2, 130.9, 133.3, 138.3, 184.2; MS (70 eV) *m/z* (%): 288 ($M^{+\cdot}$, 20), 260 (6), 122 (100). Anal. Calcd for $C_{15}H_{12}O_2S_2$: C, 62.47; H, 4.19. Found: C, 62.04; H, 4.26.

(3E,5E)-Tetrahydro-3,5-bis((pyridine-3-yl)methylene)pyran-4-one (**1h**). Yellow crystals were obtained in 86% yield, mp 192–194°C; UV (CH_2Cl_2, nm) λ_{max} 314; IR (KBr, cm^{-1}) 1672, 1616, 1272; ^1H NMR ($CDCl_3$) δ 4.86 (s, 4H), 7.18–7.70 (m, 8H), 8.50 (br s, 2H), ^{13}C NMR ($CDCl_3$) δ 68.2, 123.4, 130.4, 132.8, 134.6, 136.9, 149.9, 150.9, 187.0; MS (70 eV) *m/z* (%): 278 ($M^{+\cdot}$, 18), 117 (100), 90 (75).

Bis(arylmethylidene)thiopyranones, Typical Procedure

Ketone **2** (1 mmol) was added to the mixture of the aldehyde (2 mmol), methanol (1 mmol), $MgBr_2 \cdot OEt_2$ (1 mmol), and TEA (2 mmol) and the mixture was stirred at room temperature. The course of the reaction was monitored by TLC. At the end of the reaction the product precipitated out at once. Solids were washed by 0.5 M hydrochloric acid solution and then filtered. Recrystallization of the products by means of ethyl acetate yielded 81–91% of the desired compounds.

(3Z,5Z)-3,5-Dibenzylidene-tetrahydrothiopyran-4-one (**2a**) [3]. Yellow crystals were obtained in 91% yield, mp 142–144°C; UV (CH_2Cl_2, nm) λ_{max} 331; IR (KBr, cm^{-1}) 1599, 1444, 1269; ^1H NMR ($CDCl_3$) δ 3.84 (s, 4H), 7.30 (s, 10H), 7.72 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 30.0, 128.4, 128.7, 129.8, 133.7, 134.9, 136.6, 188.6; MS (70 eV) *m/z* (%): 292 ($M^{+\cdot}$, 27), 147 (40), 115 (100). Anal. Calcd for $C_{19}H_{16}OS$: C, 78.05; H, 5.52. Found: C, 77.63; H, 5.52.

(3Z,5Z)-3,5-Bis(4-methoxybenzylidene)-tetrahydrothiopyran-4-one (**2b**) [3]. Yellow crystals were obtained in 83% yield, mp 174–176°C; UV (CH_2Cl_2, nm) λ_{max} 330; IR (KBr, cm^{-1}) 1654, 1592, 1505, 1252; ^1H NMR ($CDCl_3$) δ 3.76 (s, 6H), 3.80 (s, 4H), 6.85 (d, 4H, $J = 9.8$ Hz), 7.30 (d, 4H, $J = 9.8$ Hz), 7.66 (s 2H); ^{13}C NMR ($CDCl_3$) δ 30.2, 55.3, 114.1, 127.5, 131.9, 136.1, 160.2, 185.4; MS (70 eV) *m/z* (%): 352 ($M^{+\cdot}$, 49), 146 (98), 103 (100). Anal. Calcd for $C_{21}H_{20}O_3S$: C, 71.56; H, 5.72. Found: C, 71.04; H, 5.56.

(3Z,5Z)-3,5-Bis(4-methylbenzylidene)-tetrahydrothiopyran-4-one (**2c**) [3]. Yellow crystals were obtained in 87% yield, mp 186–188°C; UV (CH_2Cl_2, nm) λ_{max} 325; IR (KBr, cm^{-1}) 1657, 1595, 1275; ^1H NMR ($CDCl_3$) δ 2.31 (s, 6H), 3.84 (s, 4H), 7.20–7.45 (m, 8H), 7.68 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4, 30.1, 129.1, 129.9, 132.4, 133.3, 136.8, 139.2, 185.5; MS (70 eV) *m/z* (%): 320 ($M^{+\cdot}$, 21), 305 (19), 147 (30), 130 (62), 115 (100).

(3Z,5Z)-3,5-Bis(4-chlorobenzylidene)-tetrahydrothiopyran-4-one (**2d**) [3]. Yellow crystals were obtained in 81% yield, mp 126–128°C; UV (CH_2Cl_2, nm) λ_{max} 317; IR (KBr, cm^{-1}) 1659, 1602, 1271;

^{1}H NMR ($CDCl_3$): δ 3.78 (s, 4H), 7.20–7.40 (m, 8H), 7.62 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 30.0, 129.0, 131.3, 133.5, 134.2, 135.1, 135.7, 188.5; MS (70 eV) *m/z* (%): 360 ($M^{+\cdot}$, 10), 147 (37), 115 (100).

*(3Z,5Z)-Tetrahydro-3,5-bis((E)-3-phenylallylidene)thiopyran-4-one (***2e***)* [3]. Brown crystals were obtained in 88% yield, mp 202–204°C; UV (CH_2Cl_2, nm) λ_{max} 380; IR (KBr, cm^{-1}) 1645, 1609, 1577, 1287; ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 4H), 6.80–7.80 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 28.5, 122.6, 127.3, 128.8, 129.2, 136.1, 141.9; MS (70 eV) *m/z* (%) 344 ($M^{+\cdot}$, 31), 253 (19), 141 (97), 115 (100).

*(3Z,5Z)-3,5-Bis((furan-2-yl)methylene)-tetrahydrothiopyran-4-one (***2f***)* [3]. Yellow crystals were obtained in 86% yield, mp 155–157°C; UV (CH_2Cl_2, nm) λ_{max} 372; IR (KBr, cm^{-1}) 1648, 1471, 1284, 747; ^{1}H NMR ($CDCl_3$) δ 4.04 (s, 4H), 6.40–6.58 (m, 4H), 7.35–7.49 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 29.7, 112.3, 117.4, 122.6, 129.9, 144.9, 152.0, 187.6; MS (70 eV) *m/z* (%)272 ($M^{+\cdot}$, 95), 244 (13), 137 (20), 106 (100).

*(3Z,5Z)-Tetrahydro-3,5-bis((thiophen-2-yl)methylene)thiopyran-4-one (***2g***)* [3]. Yellow crystals were obtained in 86% yield, mp 155–157°C; UV (CH_2Cl_2, nm) λ_{max} 365; IR (KBr, cm^{-1}) 1646, 1582, 1281; ^{1}H NMR ($CDCl_3$) δ 3.90 (s, 4H), 7.00–7.50 (m, 6H), 7.86 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 29.5, 127.6, 129.4, 133.2, 138.3, 187.0; MS (70 eV) *m/z* (%) 304 ($M^{+\cdot}$, 15), 153 (49), 122 (100), 121 (100). Anal. Calcd for $C_{15}H_{12}OS_3$: C, 59.18; H, 3.97. Found: C, 58.88; H, 4.02.

*(3Z,5Z)-Tetrahydro-3,5-bis((pyridine-3-yl)methylene)thiopyran-4-one (***2h***) [3].* Yellow crystals were obtained in 81% yield, mp 186–188°C; UV (CH_2Cl_2, nm) λ_{max} 301; IR (KBr, cm^{-1}) 1723, 1557, 1273; ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 4H), 7.10–7.60 (m, 8H), 8.51 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 29.7, 123.2, 130.7, 133.0, 136.0, 136.6, 149.4, 150.3, 185.0; MS (70 eV) *m/z* (%) 294 ($M^{+\cdot}$, 31), 148 (34), 117 (78), 84 (100).

CONCLUSIONS

We have established a general and efficient synthetic methodology for the preparation of 3,5-bisarylmethylidenes of heterocyclic ketones at room temperature by using an efficient medium consisted of magnesium bromide diethyl etherate, triethylamine, and methanol. In comparison with the previous procedures, the present methodology is very mild and fast. Use of no solvent, ease of operation, no special handling requirements, and more importantly, presenting the most versatile and efficient method for double crossed aldol condensation of heterocyclic ketones makes this protocol an attractive addition to the present literature archive. Application of this procedure to other heterocyclic systems and homocyclic ketones is currently under investigation and will be reported in due course.

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