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Alkaloid *N*-oxide promoted asymmetric cobalt-mediated Pauson–Khand reaction

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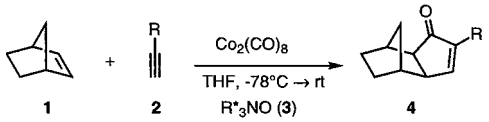
Abstract

Intermolecular cobalt-mediated Pauson–Khand reactions of norbornene derivatives **1**, **5**, **7** and **9** with various alkynes **2a–f** were carried out in the presence of chiral amine *N*-oxides **3**. Small amine *N*-oxides such as (−)-nicotine *N*1-oxide **3a** and (−)-nicotine *N*1,*N*1′-bisoxide **3b** yielded the cyclopentenones **4** with low enantioselectivities (< 10 %ee) regardless of the alkyne **2**. However, sterically more demanding amine *N*-oxides with additional hydrogen donor and/or acceptor sites such as (−)-quinine *N*-oxide (**3c**), (−)-brucine *N*-oxide (**3d**), and (+)-indolizino[3,4-*b*]quinoline *N*-oxide (**3e**) gave enantioselectivities up to 53 %ee for alkynes with tethered hydroxy moieties.

Keywords: Pauson–Khand reaction; Cobalt alkyne complexes

1. Introduction

Since the discovery of the cobalt-mediated [2 + 2 + 1] cyclization reaction in 1973, commonly known as Pauson–Khand reaction, many improvements concerning reactivity, selectivity and catalysis have been achieved [1]. In contrast, the development of asymmetric versions is still lagging behind. The first enantioselective procedure established by Pauson in 1988 used a chiral GLYPHOS ligand. The enantiomerically pure products were obtained after chromatographic separation of the two diastereomeric cobalt–alkyne–GLYPHOS complexes and subsequent cocyclization with a suitable alkene [2]. In 1996 Buchwald achieved up to 96 %ee in the first intramolecular catalytic enantioselective Pauson–Khand-type reaction using a chiral titanocene catalyst [3]. Recently, Hiroi obtained in an intramolecular reaction with catalytic amounts of $Co_2(CO)_8$ and BINAP enantioselectivities up to 94 %ee [4]. However, these methods are less successful in intermolecular Pauson–Khand reactions [3,4b,5,6]. Another approach by Greene, Riera, Pericas and others using chiral auxiliaries showed a better general efficiency in many intra- and intermolecular reactions [7]. It should be emphasized that up to now the only direct method to control the enantioselectivity of intermolecular cobalt-mediated Pauson–Khand reaction utilizes chiral amine *N*-oxides [8–10]. Since Kerr's initial report of an intermolecular reaction of a sterically demanding propargylic alcohol and norbornene in the presence of (−)-brucine *N*-oxide [8], Nicholas examined the preparation of (propargylic alcohol)$Co_2(CO)_5(PR_3)$ complexes via kinetic resolution with several chiral amine *N*-oxides [9]. In an earlier study we reported on intermolecular Pauson–Khand reactions of norbornene **1** and various terminal alkynes **2** in the presence of (−)-sparteine *N*-oxides or indolizino[3,4-*b*]quinoline *N*-oxide giving cyclopentenones **4** with enantioselectivities up to 33 %ee (Scheme 1) [10]. These results prompted us to further study the scope and limitation of alkaloid *N*-oxides



R = alkyl, Ph

(for details see Scheme 2 and Table 1)

Scheme 1.

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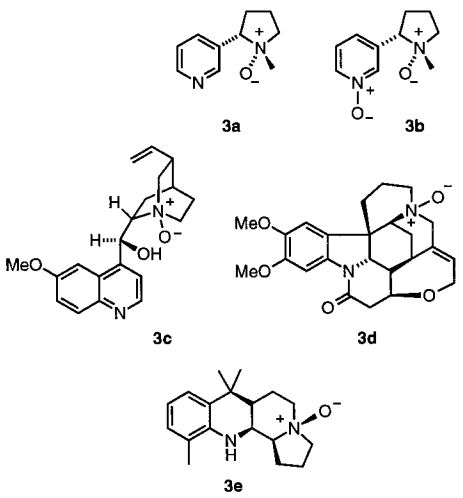


Scheme 2.

promoted Pauson–Khand reactions. The details are reported below.

2. Results and discussion

First we studied the effect of alkaloid *N*-oxides such as (−)-nicotine *N*1-oxide **3a**, (−)-nicotine *N*1,*N*1′-bisoxide (**3b**), (−)-quinine *N*-oxide (**3c**) (Scheme 2) on cobalt-mediated Pauson–Khand reactions of norbornene **1** with various terminal alkynes **2** and compared these results with reactions in the presence of (−)-brucine *N*-oxide (**3d**). As shown in Table 1, small amine *N*-oxides like nicotine *N*-oxides **3a**,**b** had only a very small effect on the stereoselectivity yielding the cyclopentenones **4** in less than 10 %ee [11]. In contrast, amine *N*-oxides with more complex structures (**3c**,**d**) showed a strong dependency between the structures of the alkyne **2** and the *N*-oxide regarding the stereoselectivity. In each series only one alkyne/*N*-oxide combination gave increased enantioselectivities (3-butyn-1-ol (**2e**) and (−)-quinine *N*-oxide (**3c**): 30 %ee; 1,1-dimethylpropynol (**2d**) and (−)-brucine *N*-oxide (**3d**): 42 %ee) [12]. Therefore the scope with regard to alkyne substrates in *N*-oxide-promoted reactions is rather limited, as can be seen in the (−)-brucine *N*-oxide series. This result agrees well with the observation by Kerr, that (−)-brucine *N*-oxide (**3d**) gave enantioselectivities up to 78 %ee only with certain 1,1-disubstituted propargylic alcohols [13].

In order to study the influence of functional groups on the stereoselectivity, Pauson–Khand reactions of substituted norbornene derivatives **5**, **7** and **9** with alkynes **2b**,**d** were performed in the presence of (−)-brucine *N*-oxide (**3d**) or (+)-indolizidino[3,4-*b*]quinoline *N*-oxide (**3e**) (Scheme 3). We found that the *endo*-norbornene ester **5** and the azanorbornene ester **7** resulted in most cases in a slight decrease of the enantiomeric excess as compared to the parent norbornene system **1**. The only exception was the (−)-brucine *N*-oxide promoted reaction of *endo*-norbornene ester **5** with propargylic alcohol **2d**, which led to a dramatic decrease of the selectivity. However, when using *endo*-1-methyl-norbornene ester **9** instead of **5** under the same conditions, the cyclopentenone **10** was obtained with improved enantioselectivity (53 %ee). Presumably, the steric effect of the 1-methyl group overrules electronic and/or steric effects of the ester groups.

Finally, we investigated intramolecular Pauson–Khand reactions of ene–yne **11** in the presence of (−)-quinine *N*-oxide (**3c**), (−)-brucine *N*-oxide (**3d**), (+)-indolizino[3,4-*b*]quinoline *N*-oxide (**3e**) or (−)-oxosparteine *N*-oxide (**3f**) (Scheme 4). Irrespective of the type of *N*-oxide, the corresponding cyclopentenone **12** was obtained with low enantioselectivities.

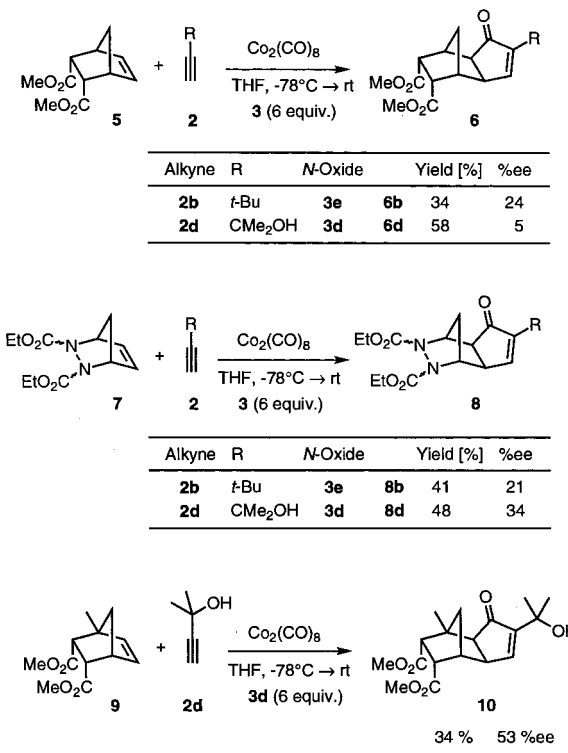
In the last few years, mechanistic aspects of the Pauson–Khand reaction have been explored both theoretically and experimentally [14]. However, the mechanism of the asymmetric induction in the cobalt-mediated intermolecular reaction is not fully un-

Table 1
Yields and enantioselectivities in the cobalt-mediated Pauson–Khand reaction of norbornene **1** with various alkynes **2** in the presence of (−)-nicotine *N*1-oxide (**3a**), (−)-nicotine *N*1,*N*1′-bisoxide (**3b**), (−)-quinine *N*-oxide (**3c**), and (−)-brucine *N*-oxide (**3d**), respectively [a,b]

Alkyne	R	Product	**3a**		**3b**		**3c**		**3d**	
2		**4**	Yield (%)	%ee	Yield (%)	%ee	Yield (%)	%ee	Yield (%)	%ee
a	Pr	**a**	75	4	69	2	28	2	75	–
b	*t*-Bu	**b**	47	10	47	10	39	6	6	–
c	Ph	**c**	81	3	82	1	65	7	38	4
d	Me_2COH	**d**	57	2	60	4	48	8	67	42
e	CH_2CH_2OH	**e**	79	2	79	2	68	30	73	2
f	CH_2OBn	**f**	41	2	48	1	27	7	62	–

[a] Reaction conditions: one equivalent of $Co_2(CO)_8$, THF, room temperature, 1 h; six equivalents of amine *N*-oxide **3**, −78 °C, 8 h; room temperature, 12 h. In all cases (−)-**4** was the major enantiomer.

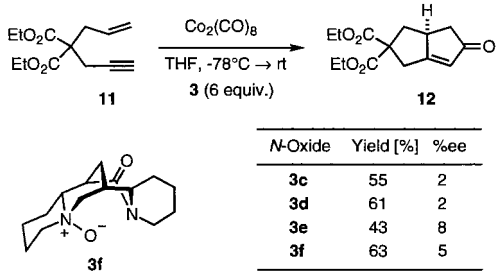
[b] Enantioselectivities of cyclopentenones **4** were determined by capillary GC using a β-cyclodextrine column. See Ref. [21].



Alkyne	R	N-Oxide		Yield [%]	%ee
2b	*t*-Bu	**3e**	**6b**	34	24
2d	CMe_2OH	**3d**	**6d**	58	5

Alkyne	R	N-Oxide		Yield [%]	%ee
2b	*t*-Bu	**3e**	**8b**	41	21
2d	CMe_2OH	**3d**	**8d**	48	34

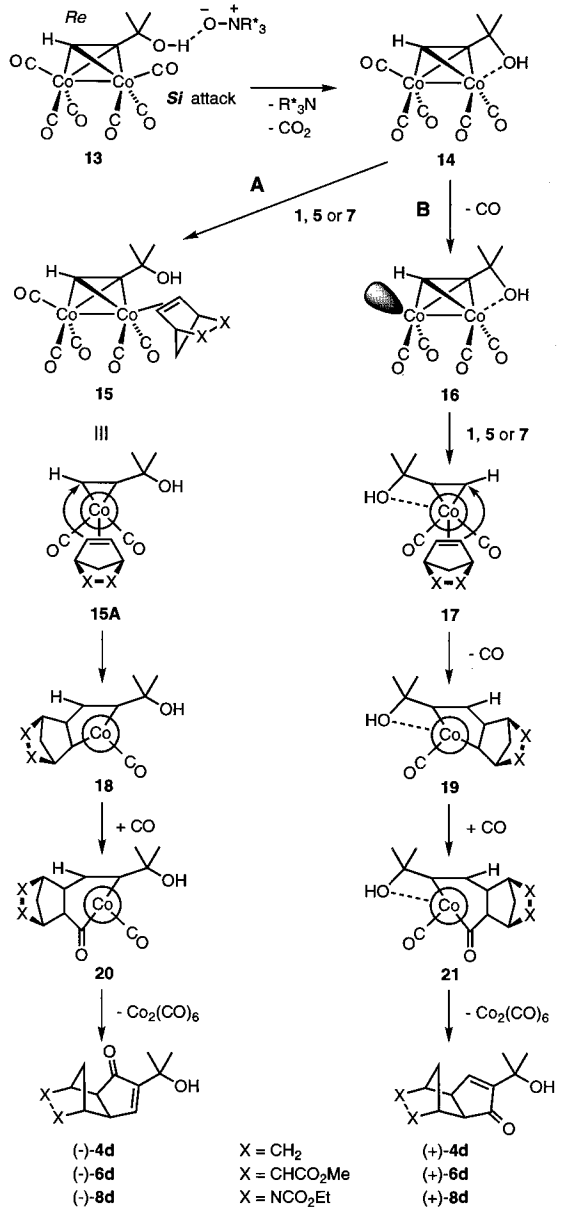
Scheme 3.



N-Oxide	Yield [%]	%ee
3c	55	2
3d	61	2
3e	43	8
3f	63	5

Scheme 4.

derstood. We observed that sterically demanding alkaloid *N*-oxides having additional sites capable of hydrogen bonding, such as (−)-quinine *N*-oxide (**3c**), (−)-brucine *N*-oxide (**3d**), and (+)-indolizino[3,4-*b*]quinoline *N*-oxide (**3e**), together with alkynes bearing a tethered alcohol moiety, result in enantioselectivities which are typically one order of magnitude higher than those from smaller *N*-oxides and 'less functionalized' alkynes. Based on these results, we propose the following mechanistic scenario (Scheme 5). Presumably amine *N*-oxides such as (−)-quinine *N*-oxide (**3c**) or (−)-brucine *N*-oxide (**3d**) are preorganized via hydrogen bonding to the cobalt alkyne complex **13**. The stability of the coordinated complex **13** probably plays a major role in controlling the stereoselectivity. This is supported by (−)-brucine *N*-oxide-promoted Pauson–Khand reactions, wherein the enantioselectivities were strongly solvent-dependent [8]. Attack of complex **13** by the amine *N*-oxide from the *Si*-face of the prochiral cobalt cluster leads to a coordinatively unsaturated cobalt complex [15]. This step is further facilitated by the tethered hydroxy group of the alkyne moiety. The Lewis basic hydroxy group then coordinates the cobalt center leading to the chelated complex **14**. There are two options conceivable for complex **14** (pathways **A** and **B**). Due to the lability of the *apical* Co–OH bond, complex **14** might undergo ligand exchange with the alkene **1**, **5** or **7**, respectively, to give the cobalt alkene complex **15** (pathway **A**) [16]. As shown in the corresponding Newman projection, **15A** insertion of the alkene takes place at the sterically less hindered Co–CH bond and thus complex **18** is formed. Further CO insertion and final extrusion of $Co_2(CO)_6$ from



Scheme 5.

complex **20** gives the cyclopentenones (−)-**4d**, (−)-**6d** and (−)-**8d** as the major enantiomers [17]. Alternatively, the Co–O bond in complex **14** might labilize the *apical* Co–CO bond at the second cobalt center, resulting in the formation of coordinatively unsaturated complex **16** (pathway **B**). Subsequent insertion of the alkene via **17** should give complex **19**, which formally can be considered as the mirror image of **18**. Consequently, complex **19** yields after CO insertion and extrusion of $Co_2(CO)_6$ the enantiomeric cyclopentenones (+)-**4d**, (+)-**6d**, and (+)-**8d**, respectively. Probably both pathways **A** and **B** contribute to the product formation and therefore only moderate selectivities could be achieved even with sterically demanding alkynes and *N*-oxides. This mechanism is in good agreement with observations by Krafft [18] and Sugihara [19], that hard Lewis bases enhance the reactivity of cobalt complexes in thermal Pauson–Khand reactions. It is further known that amines and alcohols are labilizing low-valent organotransition metal carbonyls and promote ligand exchange reactions [20]. However, as noted previously, Pauson–Khand reactions of the unsubstituted norbornene **1** in the presence of (+)-indolizino[3,4-*b*]-quinoline *N*-oxide (**3e**) yielded a higher enantioselectivity for 3,3-dimethyl-butyne (**2b**) as compared to hydroxy alkynes **2d**,**e** [10]. These results indicate that hydrogen bonding is not the only factor which determines the stereoselectivity of the intermolecular cobalt-mediated Pauson–Khand reaction.

In conclusion we have investigated further details of the alkaloid *N*-oxide promoted Pauson–Khand reaction. The results show that hydrogen bonding between alkyne and *N*-oxide plays an important role in controlling the enantioselectivity. However, there is still a great challenge to optimize the substrate/*N*-oxide interaction in order to obtain synthetically useful enantioselectivities for a broad substitution pattern. The observation that each of the alkaloid *N*-oxides **3c**,**d**,**e** gives an improved enantioselectivity only for one specific hydroxy-tethered alkyne, indicates that there is probably a subtle balance between optimal tether length and steric hindrance between cobalt–alkyne complex and amine *N*-oxide.

3. Experimental

All reactions were performed under Ar using standard Schlenck technique. Enantioselectivities were determined by capillary GC using a chiral β-cyclodextrin column. For details see Refs. [10,21]. The following compounds were prepared according to literature procedures: (−)-nicotine *N*1-oxide (**3a**) [22], (−)-nicotine *N*1,*N*1′-bisoxide (**3b**) [22], (−)-quinine *N*-oxide (**3c**) [23], (−)-brucine *N*-oxide (**3d**) [24], (+)-indolizino[3,4-*b*]quinoline *N*-oxide (**3e**) [10], (−)-oxosparteine *N*-oxide (**3f**) [10], diethyl allyl-prop-2-ynemalonate (**11**) [25].

3.1. General procedure for intermolecular Pauson–Khand reactions in the presence of chiral amine N-oxides

To a solution of alkyne **2** (0.13 mmol) in THF (10 ml) was added $Co_2(CO)_8$ (48.0 mg, 0.13 mmol) and the resulting mixture was stirred for 1 h at room temperature (r.t.). The solution was cooled to −78 °C and then were added the norbornene derivative (**1**, **5**, **7**, **9**) (0.15 mmol) and amine *N*-oxide (0.75 mmol). After stirring for 8 h at −78 °C, the mixture was warmed to r.t. overnight. To the blue solution was added SiO_2 (1 g) and the solvent was removed in vacuo. The crude product was purified by flash chromatography on SiO_2. Spectroscopic data of the cyclopentenones **4a**–**f** and **10** are described in Refs. [10,14c].

*3.2. Dimethyl (1RS,2SR,3SR,4SR,5SR,9SR)-7-tert-butyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (**6b**)*

Flash chromatography (hexanes–EtOAc 5:1) yielded 13 mg (32%) of a colorless oil; IR (film) 1739, 1698; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.15 (d, $J = 2.9$ Hz, 1H, 8-H), 3.66, 3.64 (s, 6H, CO_2CH_3), 3.36–3.34 (m, 1H, 9-H), 3.16 (dd, $J = 4.2/11.5$ Hz, 1H, 3-H), 3.06 (dd, $J = 3.7/11.5$ Hz, 1H, 2-H), 2.73–2.72 (m, 1H, 1-H), 2.59–2.58 (m, 1H, 5-H), 2.48 (s, 1H, 4-H), 1.23–1.19 (m, 10H, 10-H_a, 2′-H), 1.11 (d, $J = 10.9$ Hz, 1H, 10-H_b); ^{13}C-NMR (100 MHz, $CDCl_3$) 209.7 (C-6), 172.8, 172.1 (CO_2CH_3), 157.8 (C-8), 156.5 (C-7), 51.7, 51.4 (CO_2CH_3), 49.4 (C-5), 46.7 (C-2), 45.8 (C-3), 42.7 (C-1), 41.4 (C-9), 40.5 (C-4), 32.2 (C-10), 31.9 (C-1′), 28.3 (C-2′); EIMS m/z (%) = 320 (5) [M^+], 305 (3), 289 (3), 260 (4), 195 (25), 179 (19), 166 (18), 145 (64), 113 (94), 99 (22), 81 (36), 66 (100); HRMS (EI): m/z 320.1620 [M^+, 320.1623 calc. for $C_{18}H_{24}O_5$]. Anal. Found: C, 67.53; H, 7.51. Calc. for $C_{18}H_{24}O_5$: C, 67.48. H, 7.55%.

*3.3. Dimethyl (1RS,2SR,3SR,4SR,5SR,9SR)-7-(2-hydroxyisopropyl)-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (**6d**)*

Flash chromatography (hexanes–EtOH 7:1) yielded 24 mg (58%) of a colorless oil; IR (film) 3477, 1737, 1692, 1686; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.29 (s, 1H, 8-H), 3.74–3.67 (m, 7H, CO_2CH_3, OH), 3.42 (s, 1H, 9-H), 3.17 (dd, $J = 4.4/11.7$ Hz, 1H, 3-H), 3.08 (dd, $J = 3.8/11.7$ Hz, 1H, 2-H), 2.74–2.70 (m, 2H, 1-H, 5-H), 2.51 (s, 1H, 4-H), 1.40 (s, 6H, 2′-H), 1.24, 1.14 (d, $J = 11.0$ Hz, 2H, 10-H_a, 10-H_b); ^{13}C-NMR (100 MHz, $CDCl_3$) 211.1 (C-6), 172.0, 171.9 (CO_2CH_3), 156.9 (C-8), 154.8 (C-7), 69.6 (C-1′), 51.8, 51.5 (CO_2CH_3), 49.3 (C-5), 46.6 (C-2), 45.7 (C-3), 42.5 (C-1), 41.6 (C-9), 41.2 (C-4), 32.3 (C-10), 28.7 (C-2′); EIMS m/z (%) 322 (5)

[M^+], 307 (100), 291 (24), 275 (63), 247 (11), 233 (6), 215 (21); HRMS (EI) m/z 322.1410 [M^+, 322.1416 calc. for $C_{17}H_{22}O_6$]. Anal. Found: C, 63.15; H, 6.91. Calc. for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88%.

3.4. Diethyl (1RS,4SR,5SR,9SR)-2,3-diaza-7-tert-butyl-6-oxotricyclo[5.2.1.$0^{5,9}$]dec-7-ene-2,3-dicarboxylate (**8b**)

Flash chromatography (hexanes–isopropanol 1:1) yielded 19 mg (41%) of a colorless oil; IR (film) 1746, 1702, 1687; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.14 (s, 1H, 8-H), 4.74–4.41 (br s, 2H, 4-H, 1-H), 4.31–4.13 (m, 4H, OCH_2CH_3), 3.18–3.06 (br s, 1H, 5-H), 2.81–2.69 (br s, 1H, 9-H), 1.52, 1.41 (d, 2H, $J = 11.2$ Hz, 10-H_a, 10-H_b), 1.30–1.26 (m, 6H, OCH_2CH_3), 1.17 (s, 9H, $C(CH_3)_3$); ^{13}C-NMR (100 MHz, $CDCl_3$) 205.4 (br, C-6), 158.9 (C-7), 158.0 (br, CO), 153.3 (C-8), 62.7, 62.3 (OCH_2CH_3), 61.4, 59.7 (br, C-1, C-4), 52.8, 51.2 (br, C-9), 46.5 (br, C-5), 32.1 ($C(CH_3)_3$), 30.8 (C-10), 28.1 ($C(CH_3)_3$), 14.4, 14.1 (OCH_2CH_3); EIMS m/z (%) 350 (10) [M^+], 305 (3), 240 (8), 213 (35), 169 (7), 141 (100), 125 (8), 123 (7), 97 (37), 91 (6), 77 (5), 69 (78); HRMS (EI) m/z 350.1835 [M^+, 350.1842 calc. for $C_{18}H_{26}N_2O_5$]. Anal. Found: C, 61.78; H, 7.49; N, 7.72. Calc. for $C_{18}H_{26}N_2O_5$: C, 61.70; H, 7.48; N, 7.99%.

3.5. Diethyl (1RS,4SR,5SR,9SR)-2,3-diaza-7-(2-hydroxyisopropyl)-6-oxotricyclo[5.2.1.$0^{5,9}$]dec-7-ene-2,3-dicarboxylate (**8d**)

Flash chromatography yielded 22 mg (48%) of a colorless oil; IR (film) 3467, 1749, 1702; ^{1}H-NMR (400 MHz, $CDCl_3$) 7.31 (s, 1H, 8-H), 4.81–4.40 (br s, 2H, 4-H, 1-H), 4.31–4.12 (m, 4H, OCH_2CH_3), 3.28 (s, 1H, OH), 3.27–3.05 (br s, 1H, 5-H), 2.88–2.76 (br s, 1H, 9-H), 1.54, 1.44 (d, $J = 11.1$ Hz, 2H, 10-H_a, 10-H_b), 1.38 (s, 6H, $C(CH_3)_2OH$), 1.29–1.19 (m, 6H, OCH_2CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) 205.4 (br, C-6), 157.2 (br, CO), 155.3 (C-8), 153.3 (br, C-7), 68.6 ($C(CH_3)_2OH$), 61.8 (OCH_2CH_3), 60.3, 58.8 (br, C-1, C-4), 51.9 (br, C-9), 45.0 (br, C-5), 29.9 (C-10), 27.5, 27.4 ($C(CH_3)_2OH$), 13.5 (OCH_2CH_3); EIMS m/z (%) 352 (7) [M^+], 307 (3), 293 (2), 262 (1), 213 (32), 169 (9), 141 (100), 125 (10), 122 (33), 97 (43), 84 (12), 69 (87); HRMS (EI) m/z 352.1628 [M^+, 352.1634 calc. for $C_{17}H_{24}N_2O_6$]. Anal. Found: C, 58.03; H, 6.85; N, 7.80. Calc. for $C_{17}H_{24}N_2O_6$: C, 57.94; H, 6.86; N, 7.95%.

3.6. General procedure for intramolecular Pauson–Khand reactions in the presence of chiral amine N-oxides

To a solution of ene–yne **11** (238 mg, 1.00 mmol) in THF (5 ml) was added $Co_2(CO)_8$ (342 mg, 1.00 mmol) and the resulting mixture was stirred for 30 min at r.t. The solution was cooled to −78 °C and then amine *N*-oxide (6.00 mmol) was added. After stirring for 8 h at −78 °C, the mixture was warmed to room temperature overnight. The crude product was purified by flash chromatography on SiO_2 (eluent: hexanes–EtOAc 1:1). Spectroscopic data of the cyclopentenone **11** are in accord with Ref. [26].

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References

[1] (a) K.M. Brummond, J.L. Kent, Tetrahedron 56 (2000) 1657;
(b) A.J. Fletcher, S.D.R. Christie, J. Chem. Soc. Perkin Trans. 1 (2000) 1657;
(c) Y.K. Chung, Coord. Chem. Rev. 188 (1999) 297;
(d) N. Jeong, in: M. Beller, C. Bolm (Eds.), Transition Metals in Organic Chemistry, vol. 1, Wiley-VCH, Weinheim, 1998, p. 560;
(e) O. Geis, H.-G. Schmalz, Angew. Chem. Int. Ed. Engl. 37 (1998) 911;
(f) S.T. Ingate, J. Marco-Contelles, Org. Prep. Proced. Int. 30 (1998) 121;
(g) S.L. Buchwald, F.A. Hicks, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, vol. 2, Springer, Berlin, 1999, p. 491.

[2] (a) P. Bladon, P.L. Pauson, H. Brunner, R. Eder, J. Organomet. Chem. 355 (1988) 449;
(b) P. Bladon, P.L. Pauson, Tetrahedron Asym. 1 (1990) 711;
(c) A.M. Hay, W.J. Kerr, G.G. Kirk, D. Middlemiss, Organometallics 14 (1995) 4986.

[3] (a) F.A. Hicks, S.L. Buchwald, J. Am. Chem. Soc. 118 (1996) 11688;
(b) F.A. Hicks, S.L. Buchwald, J. Am. Chem. Soc. 121 (1999) 7026;
(c) F.A. Hicks, N.M. Kablaoui, S.L. Buchwald, J. Am. Chem. Soc. 121 (1999) 5881.

[4] (a) K. Hiroi, T. Watanabe, R. Kawagishi, I. Abe, Tetrahedron Lett. 41 (2000) 891;
(b) K. Hiroi, T. Watanabe, R. Kawagishi, I. Abe, Tetrahedron Asym. 11 (2000) 797.

[5] V. Derdau, S. Laschat, I. Dix, P.G. Jones, Organometallics 18 (1999) 3859.

[6] T. Shibata, K. Takagi, J. Am. Chem. Soc. 122 (2000) 9852.

[7] (a) J. Adrio, J.C. Carretero, J. Am. Chem. Soc. 121 (1999) 7411;
(b) E. Montenegro, A. Moyano, M.A. Pericas, A. Riera, A. Alvarez-Larena, J.F. Piniella, Tetrahedron Asym. 10 (1999) 457;
(c) J. Balsells, A. Moyano, M.A. Pericas, A. Riera, Org. Lett. 1 (1999) 1981;
(d) E. Montenegro, M. Poch, A. Moyano, M.A. Pericàs, A. Riera, Tetrahedron Lett. 39 (1998) 335;
(e) X. Verdaguer, J. Vàzquez, G. Fuster, V. Bernardes-Gènisson, A.E. Greene, A. Moyano, M.A. Pericàs, A. Riera, J. Org. Chem. 63 (1998) 7037;

(f) E. Montenegro, M. Poch, A. Moyano, M.A. Pericas, A. Riera, Tetrahedron 53 (1997) 8651;
(g) S. Fonquerna, A. Moyano, M.A. Pericas, A. Riera, J. Am. Chem. Soc. 119 (1997) 10225.
[8] W.J. Kerr, G.G. Kirk, D. Middlemiss, Synlett (1995) 1085.
[9] N.E. Carpenter, K.M. Nicholas, Polyhedron 18 (1999) 2027.
[10] V. Derdau, S. Laschat, P.G. Jones, Heterocycles 48 (1998) 1445.
[11] (a) I.A. O'Neil, N.D. Miller, J. Peake, J.V. Barkley, C.M.R. Low, S.B. Kalindjian, Synlett (1993) 515;
(b) I.A. O'Neil, N.D. Miller, J.V. Barkley, C.M.R. Low, S.B. Kalindjian, Synlett (1995) 617.
[12] When less than six equivalents of amine *N*-oxide were used, the yields of the cyclopentenones decreased dramatically.
[13] (a) W.J. Kerr, D.M. Lindsay, E.M. Rankin, J.S. Scott, S.P. Watson, Tetrahedron Lett. 41 (2000) 3229;
(b) D.R. Carbery, W.J. Kerr, D.M. Lindsay, J.S. Scott, S.P. Watson, Tetrahedron Lett. 41 (2000) 3235.
[14] (a) F. Robert, A. Milet, Y. Gimbert, D. Konya, A.E. Greene, J. Am. Chem. Soc. 123 (2001) 5396;
(b) M. Yamanaka, E. Nakamura, J. Am. Chem. Soc 123 (2001) 1703;
(c) V. Derdau, S. Laschat, P.G. Jones, Eur. J. Org. Chem. (2000) 681;
(d) J. Castro, A. Moyano, M.A. Pericas, A. Riera, A. Alvarez-Larena, J.F. Piniella, J. Am. Chem. Soc. 122 (2000) 7944;
(e) J. Balsells, J. Vazquez, A. Moyano, M.A. Pericas, A. Riera, J. Org. Chem. 65 (2000) 7291.
[15] J.-K. Shen, Y.-C. Gao, Q.-Z. Shi, F. Basolo, Organometallics 8 (1989) 2144.
[16] Very recent DFT calculations by Gimbert, Greene and Milet indicate that the alkene reacts through facile pseudorotation from an *apical* position with one of the lowest activation energy for C–C bond formation. For details, see: T.J.M. de Bruin, A. Milet, F. Robert, Y. Gimbert, A.E. Greene, J. Am. Chem. Soc. 123 (2001) 7184.
[17] For stereochemical assignment of the Pauson–Khand products see Ref. [14d].
[18] M.E. Krafft, L.V.R. Bonaga, C. Hirosawa, J. Org. Chem. 66 (2001) 3004.
[19] (a) T. Sugihara, M. Yamaguchi, M. Nishizawa, Chem. Eur. J. 7 (2001) 1589;
(b) T. Sugihara, M. Yamada, H. Ban, M. Yamaguchi, C. Kaneko, Angew. Chem. Int. Ed. Engl. 36 (1997) 2801.
[20] (a) R.J. Dennenberg, D.J. Darensbourg, Inorg. Chem. 11 (1972) 72;
(b) J.D. Atwood, T.L. Brown, J. Am. Chem. Soc. 98 (1976) 3160;
(c) D.J. Darensbourg, R.L. Kump, Inorg. Chem. 17 (1978) 2680.
[21] W.A. König, B. Gehrck, D.H. Hochmuth, C. Mlynek, H. Hopf, Tetrahedron Asym. 5 (1994) 347.
[22] E.C. Taylor, N.E. Boyer, J. Org. Chem. 24 (1959) 275.
[23] E. Wenkert, J.S. Bindra, C.-J. Chang, D.W. Cochran, F.M. Schell, Acc. Chem. Res. 17 (1974) 46.
[24] (a) E. Wenkert, H.T.A. Cheung, H.E. Gottlieb, J. Org. Chem. 43 (1978) 1099;
(b) E. Wenkert, H.T.A. Cheung, H.E. Gottlieb, Orient. J. Chem. 8 (1992) 142.
[25] N. Chatani, T. Takeyasu, N. Horiuchi, T. Hanafusa, J. Org. Chem. 53 (1988) 3539.
[26] S.C. Berk, R.B. Grossman, S.L. Buchwald, J. Am. Chem. Soc. 116 (1994) 8593.