Formation of Chiral β-Lactams by Photocyclisation of Achiral *N,N*-Diisopropylarylglyoxylamides in their Chiral Crystalline Form

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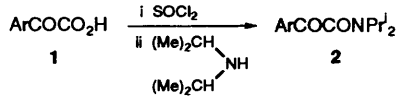
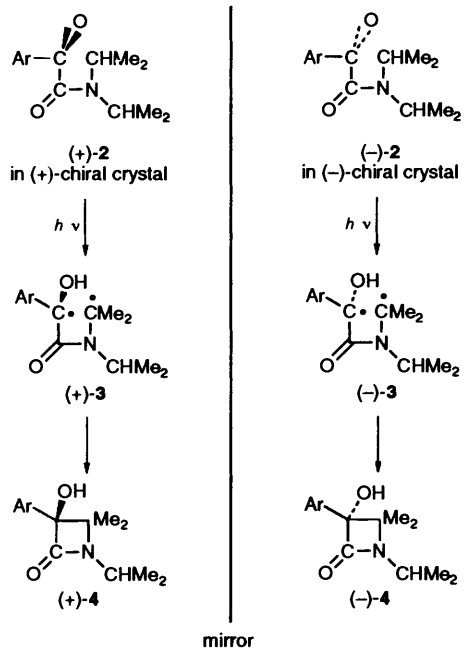
A variety of *N,N*-diisopropylarylglyoxylamides formed chiral crystals in which the originally symmetrical molecules were arranged in a chiral form. Photoreaction of the chiral crystals gave optically active β-lactam derivatives.

Earlier, we reported that, upon irradiation, the chiral crystals formed by *N,N*-diisopropylphenylglyoxylamide **2a** in which the

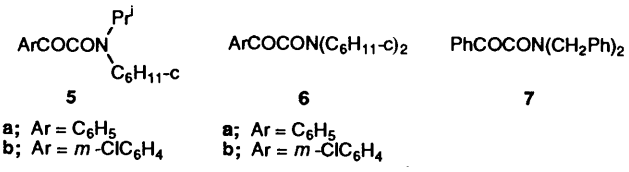


symmetrical molecules are arranged in an achiral form gives the optically active β-lactam derivative, 3-hydroxy-1-isopropyl-4,4-dimethyl-3-phenylazetidin-2-one **4a** (see Scheme 1 and entry 1 in Table 1).[1,2] Such a reaction demonstrates the initiation of chirality. X-Ray crystal structure analysis of the chiral crystals showed that the CO–CO group of **2a** is twisted *ca.* 90° around the central single bond, thus forcing the symmetrical molecule of **2a** to exhibit chirality in the crystal:[2] this chirality is frozen by photocyclisation to give **4a**. Other examples of initiation of chirality in crystals have been described.[3,4]



Scheme 1

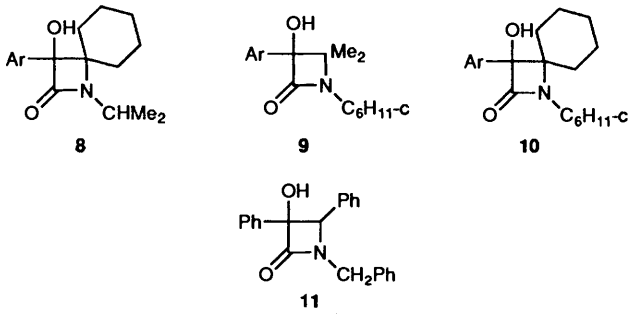
We studied, in detail, the relationship between the formation of chiral crystals and the type of substituent on **2**, and have shown that chiral crystals are formed when the Ar group of **2** is phenyl (**2a**) or a *meta*-substituted phenyl (**2b–d**), but that racemic crystals are formed when Ar is a *para*-substituted phenyl (**2e–g**). In addition, when **2** has an *o*-methyl **2j** or *m,p*-dimethylphenyl group **2k** it also forms chiral crystals, but when **2** has an *o*-chloro **2h**, *o*-bromo **2i** or *m,m*-dimethylphenyl group **2l** it forms a racemic crystal. Crystals of **2** (**2a–d**, **2j**, **2k**) gave optically active β-lactam derivatives upon irradiation (Table 1). Only *N,N*-diisopropyl oxo amides **2** gave chiral crystals with oxo amides **5**, **6** and **7** forming racemic crystals (Table 2).



The oxo amides, **2b–l** were prepared according to a reported method:[1,2] namely, chlorination of the arylglyoxylic acid **1**[5–7] with $SOCl_2$ followed by reaction with diisopropylamine or dialkylamine. Similarly, **5**, **6** and **7** were prepared from the corresponding amine and arylglyoxylic acid **1**. All the oxo amides form colourless crystals with sharp melting points (Tables 1 and 2). The chirality or otherwise of the crystals was determined empirically by irradiation of a powdered piece of one. Crystals which upon irradiation gave (+)-lactams were tentatively designated as (+)-crystals, whilst those which formed (−)- and *rac*-β-lactams were designated as (−)- and racemic crystals, respectively.

(+) and (−)-Crystals were prepared in large quantities by seeding the oxo amide during its recrystallisation with an appropriate crystal.

Photoirradiations of powdered oxo amides were carried out at room temperature. Chemical and optical yields of products are summarised in Tables 1 and 2. Oxo amides which have a *meta*-substituted phenyl **2b–d** and an *o*-tolyl group **2j** formed chiral crystals and their irradiation gave optically active β-lactams in high chemical and optical yields (entries 2–4 and 10 in Table 1). However, the oxo amides which have a *para*-substituted phenyl group (**2e–g**) or an *o*-chloro- **2h** or *o*-bromo-phenyl group **2i** formed racemic crystals and their irradiation gave the corresponding racemic β-lactam (entries 5–9 in Table 1).



It is interesting, however, that **2k** substituted with an *m,p*-dimethylphenyl group forms chiral crystals and its irradiation

Table 1 Chemical and optical yields of **4** obtained by photoirradiation of **2** in the solid state

	2					Product 4						
			Analysis % Found (Calc.)					Analysis % Found (Calc.)				
Entry	Ar	M.p. (°C)[a]	C	H	N	Irradiation time (h)	Yield (%)	M.p. (°C)	C	H	N	$[\alpha]_D$	(*c*, solvent)	Optical purity (% ee)
1 **a**	C_6H_5	124–126[9]				40	74	149–150				+123	(0.50, $CHCl_3$)	93[c]
2 **b**	*m*-ClC_6H_4	118	$C_{14}H_{18}ClNO_2$			10	75	144–145	$C_{14}H_{18}ClNO_2$			−107	(0.84, MeOH)	100[c]
			63.1	7.05	5.1				62.95	6.85	4.8			
			(62.80	6.78	5.23)				(62.80	6.78	5.23)			
3 **c**	*m*-BrC_6H_4	120–121	$C_{14}H_{18}BrNO_2$			5	97	142–144	$C_{14}H_{18}BrNO_2$			−79	(0.54, MeOH)	96[c]
			54.1	5.8	4.8				53.7	5.9	4.7			
			(53.86	5.81	4.49)				(53.86	5.81	4.49)			
4 **d**	*m*-MeC_6H_4	96–97	$C_{15}H_{21}NO_2$			7	63	118–120	$C_{15}H_{21}NO_2$			+101	(0.43, MeOH)	91[c]
			72.7	8.55	6.05				72.8	8.9	5.9			
			(72.84	8.56	5.66)				(72.84	8.56	5.66)			
5 **e**	*p*-ClC_6H_4	75–76	$C_{14}H_{18}ClNO_2$			5	50	191–192	$C_{14}H_{18}ClNO_2$			0		0
			63.1	6.8	5.05				62.6	6.83	4.85			
			(62.80	6.78	5.23)				(62.80	6.8	5.23)			
6 **f**	*p*-BrC_6H_4	104–105	$C_{14}H_{18}BrNO_2$			12	65	203–205	$C_{14}H_{18}BrNO_2$			0		0
			53.8	5.85	4.9				53.7	5.8	4.3			
			(53.86	5.81	4.49)				(53.86	5.81	4.49)			
7 **g**	*p*-MeC_6H_4	54–55	$C_{15}H_{21}NO_2$			5	60	163–164	$C_{15}H_{21}NO_2$			0		0
			72.7	8.7	5.7				72.8	8.1	5.2			
			(72.84	8.56	5.66)				(72.84	8.56	5.66)			
8 **h**	*o*-ClC_6H_4	61–63	$C_{14}H_{18}ClNO_2$			24	42	190–192	$C_{14}H_{18}ClNO_2$			0		0
			63.0	6.9	4.9				62.4	6.7	5.0			
			(62.80	6.78	5.23)				(62.80	6.78	5.23)			
9 **i**	*o*-BrC_6H_4	80–81	$C_{14}H_{18}BrNO_2$			24	48	185–187	$C_{14}H_{18}BrNO_2$			0		0
			53.6	5.55	4.3				53.9	5.9	4.5			
			(53.86	5.81	4.49)				(53.86	5.81	4.49)			
10 **j**	*o*-MeC_6H_4	97–99	$C_{15}H_{21}NO_2$			10	54	163–163.5	$C_{15}H_{21}NO_2$			−158	(0.40, MeOH)	92[d]
			73.1	8.9	5.6				73.0	8.7	5.9			
			(72.84	8.56	5.66)				(72.84	8.56	5.66)			
11 **k**	*m,p*-$Me_2C_6H_3$	86–87	$C_{16}H_{23}NO_2$			5	62	159–160	$C_{16}H_{23}NO_2$			+70	(0.18, MeOH)	54[e]
			73.5	9.0	5.2				73.4	9.1	5.45			
			(73.53	8.87	5.36)				(73.53	8.87	5.36)			
12 **l**	*m,m*-$Me_2C_6H_3$	74–75	$C_{16}H_{23}NO_2$			5	74	137–138	$C_{16}H_{23}NO_2$			0		0
			73.5	9.1	5.2				73.5	9.0	5.3			
			(73.53	8.87	5.36)				(73.53	8.87	5.36)			

[a] All crystals were colourless prisms. [b] All are isolated yields. [c] All optical purities were determined by HPLC using a column containing the optically active solid-phase Chiralpak As. [d] Chiralcel OD[8] was used. [e] Chiralcel OC was used.

gives optically active **4k**, while **2l**, which is substituted with a *m,m*-dimethylphenyl group, forms racemic crystals. These data show that the formation of a chiral crystal is delicately dependent on the structure of the aryl group of **2**.

That, in the chiral crystal, the oxo amide molecule may be twisted around the central single bond of the CO–CO group thus forcing it to arrange in a chiral form (see Scheme 1), was proven for **2a** by an X-ray structure analysis of the chiral form.[2] Photocyclisation of **2** in a chiral crystal may proceed *via* the chiral biradical **3** to give the finally optically active **4** (Scheme 1). Since molecules are packed tightly and regularly in the crystal, chemical yields of the photoreaction is very high, although the enantioselectivity is not very high particularly in the case of **2k**.

During the formation of racemic crystals (entries 5–9 and 12 in Table 1), (+)- and (−)-molecules of oxo amide are probably arranged in a 1 : 1 ratio in the crystal, and a racemic β-lactam is produced by photoreaction. This idea is supported by X-ray crystal analysis of **2e**.* Nevertheless, it is still valuable to produce the β-lactam by the photoreaction of **2** in the crystal, since irradiation of the oxo amide in solution gives racemic β-lactam in low yields.[9]

Two isopropyl groups in **2** are necessary for the formation of chiral crystals, since oxo amides which have only one isopropyl group, such as **5a** and **5b** and those which have no isopropyl groups, such as **6a**, **6b** and **7**, form racemic crystals and on irradiation give the corresponding racemic β-lactams (Table 2). It is interesting, however, that **5a** and **5b** react to give **8** and **9**, respectively. This shows that the cyclohexyl and isopropyl groups are arranged in a position close to the carbonyl group which abstracts a hydrogen. The reason why **5**, **6**, and **7** do not form chiral crystals will be clarified by a future X-ray structure study.

Experimental

Materials.—The oxo amides, *N,N*-diisopropylarylglyoxylamides **2b–l** were prepared according to the reported method[1] from diisopropylamine and the arylglyoxylic acid **1**, which had been synthesised by a reported method.[5–7] The other oxo amides **5**, **6** and **7** were also prepared from the corresponding amine and **1** according to the method described above. Both **2a** and **7** were prepared according to the literature.[9] The oxoamides are all crystalline materials and were purified by recrystallisation from MeOH. Chiral crystals of **2b–d** and **2j–k** were obtained in large quantities by the addition of one piece of chiral crystal during the recrystallisation of these compounds from MeOH. Melting points, uncorrected, and

* X-Ray structure analysis showed that the racemic crystal of **2e** has a symmetric centre and contains its twisted (+)- and (−)-molecules in a 1 : 1 ratio.[8]

Table 2 Chemical yield of **8**, **9**, **10**, **11** obtained by photoirradiation of **5**, **6**, **7** in the solid state

	Oxo amide						Product					
			Analysis % Found (Calc.)							Analysis % Found (Calc.)			
Entry		M.p. (°C)[a]	C	H	N	Irradiation time (h)		Yield (%)[b]	M.p. (°C)	C	H	N	$[\alpha]_D$
1	**5a**	72–73	$C_{17}H_{23}NO_2$			23	**8**	20	194–196	$C_{17}H_{23}NO_2$			0
			74.4	8.5	4.90					74.8	8.8	5.1	
			(74.69	8.48	5.12)					(74.69	8.48	5.12)	
2	**5b**	91–92	$C_{17}H_{22}NO_2Cl$			24	**9**	51	151–152	$C_{17}H_{22}NO_2Cl$			0
			66.5	7.3	4.3					66.4	7.2	4.9	
			(66.33	7.20	4.55)					(66.33	7.20	4.55)	
3	**6a**	119–120	$C_{20}H_{27}NO_2$			15	**10a**	57	183–185	$C_{20}H_{27}NO_2$			0
			76.4	9.0	4.25					76.3	8.8	4.4	
			(76.64	8.68	4.47)					(76.64	8.68	4.47)	
4	**6b**	121–122	$C_{20}H_{26}NO_2Cl$			32	**10b**	29	219–220	$C_{20}H_{27}NO_2$			0
			69.1	7.7	3.9					69.0	7.8	3.75	
			(69.05	7.53	4.03)					(69.05	7.53	4.03)	
5	**7**	83–84				15	**11**	67	100–102				0

[a] **5a**, **5b**, **8a** and **10** were colourless prisms, **8b** was colourless needles. [b] All are isolated yields.

elemental analytical data of **2**, **5**, **6** and **7** are shown in Tables 1 and 2.

The oxo amides, powdered and kept in agate mortar, were irradiated in the air using a 400 W high-pressure Hg-lamp for the period shown in Tables 1 and 2, with occasional grinding with a pestle. Reaction products were isolated by column chromatography on silica gel using AcOEt–toluene (1 : 9) as an eluent and were purified by recrystallisation from benzene. Optical purities were determined by HPLC, using a column containing the optically active solid phase Chiralpak As, Chiralcel OD or Chiralcel OC.* $[\alpha]_D$ Values recorded in 10^{-1} deg cm^2 g^{-1}. For example, irradiation of a powdered chiral crystal of **2b** (0.15 g, 0.56 mmol) for 10 h gave, after purification, (−)-**4b** of 100% e.e. {0.11 g, 75% yield, m.p. 144–145 °C, $[\alpha]_D$ −107 (*c* 0.84, MeOH)}. Yields, melting points, elemental analytical data, $[\alpha]_D$ values, and optical purities of the photocyclisation products are shown in Tables 1 and 2.

IR, ^{1}H *NMR and Mass Spectral Data for Compounds* **2b–l**, **4b–l**, **5a**, **5b**, **6a**, **6b**, **8**, **9**, **10a** *and* **10b**.—^{1}H NMR spectra were recorded at 60 MHz on a JEOL JNM-PMX 60 for solutions in $CDCl_3$ using tetramethylsilane as internal standard. *J* Values are given in Hz.

2b. ν_{max}(Nujol)/cm^{-1} 1690 and 1650; δ_H 1.22 (d, *J* 7, 6 H, $CHMe_2$), 1.60 (d, *J* 7, 6 H, $CHMe_2$) 3.63 (sep., *J* 7, 1 H, N-CH) and 7.23–8.00 (m, 5 H, ArH); *m/z* 268 (M^+).

2c. ν_{max}(Nujol)/cm^{-1} 1680 and 1640; δ_H 1.18 (d, *J* 7, 6 H, $CHMe_2$), 1.56 (d, *J* 7, 6 H), 3.63 (sep., *J* 7, 1 H, N–CH) and 7.20–8.17 (m, 5 H, ArH); *m/z* 312 (M^+).

2d. ν_{max}(Nujol)/cm^{-1} 1680 and 1640; δ_H 1.16 (d, *J* 7, 6 H, $CHMe_2$), 1.58 (d, *J* 7, 6 H, $CHMe_2$), 2.43 (s, 3 H, CH_3), 3.60 (sep., *J* 7, 1 H, N–CH) and 7.23–8.00 (m, 5 H, ArH); *m/z* 248 (M^+).

2e. ν_{max}(Nujol)/cm^{-1} 1680 and 1630; δ_H 1.23 (d, *J* 7, 6 H, $CHMe_2$), 1.60 (d, *J* 7, 6 H, $CHMe_2$), 3.63 (sep., *J* 7, 1 H, N–CH), 7.47 (d, *J* 8, 2 H, ArH) and 7.87 (d, *J* 8, 2 H, ArH); *m/z* 268 (M^+).

2f. ν_{max}(Nujol)/cm^{-1} 1675 and 1630; δ_H 1.18 (d, *J* 7, 6 H, $CHMe_2$), 1.59 (d, *J* 7, 6 H, $CHMe_2$), 3.63 (sep., *J* 7, N–CH), 7.11 (d, *J* 9, 2 H, ArH) and 7.25 (d, *J* 9, 2 H, ArH); *m/z* 312 (M^+).

2g. ν_{max}(Nujol)/cm^{-1} 1675 and 1640; δ_H 1.15 (d, *J* 7, 6 H, $CHMe_2$), 1.56 (d, *J* 7, 6 H, $CHMe_2$), 2.40 (s, 3 H, CH_3), 3.58 (sep., *J* 7, 1 H, N–CH), 7.26 (d, *J* 8, 2 H, ArH) and 7.76 (d, *J* 8, 2 H, ArH); *m/z* 248 (M^+).

2h. ν_{max}(Nujol)/cm^{-1} 1670 and 1645; δ_H 1.24 (d, *J* 7, 6 H, $CHMe_2$), 1.53 (d, *J* 7, 6 H, $CHMe_2$), 3.72 (sep., *J* 7, 1 H, N–CH) and 7.10–8.00 (m, 4 H, ArH); *m/z* 268 (M^+).

2i. ν_{max}(Nujol)/cm^{-1} 1670 and 1635; δ_H 1.26 (d, *J* 7, 6 H, $CHMe_2$), 1.51 (d, *J* 7, 6 H, $CHMe_2$), 3.60 (sep., *J* 7, 1 H, N–CH) and 7.13 ~ 7.97 (m, 4 H, ArH); *m/z* 312 (M^+).

2j. ν_{max}(Nujol)/cm^{-1} 1670 and 1640; δ_H 1.18 (d, *J* 7, 6 H, $CHMe_2$), 1.56 (d, *J* 7, 6 H, $CHMe_2$), 2.65 (s, 3 H, CH_3), 3.63 (sep., *J* 7, 1 H, N–CH) and 7.00–7.97 (m, 5 H, ArH); *m/z* 248 (M^+).

2k. ν_{max}(Nujol)/cm^{-1} 1660 and 1635; δ_H 1.14 (d, *J* 7, 6 H, $CHMe_2$), 1.57 (d, *J* 7, 6 H, $CHMe_2$), 2.32 (s, 6 H, CH_3), 3.62 (sep., *J* 7, 1 H, N–CH), 7.19 (d, *J* 8, 1 H, ArH), 7.61 (d, *J* 8, 1 H, ArH) and 7.70 (s, 1 H ArH); *m/z* 262 (M^+).

2l. ν_{max}(Nujol)/cm^{-1} 1660 and 1630; δ_H 1.16 (d, *J* 7, 6 H, $CHMe_2$), 1.59 (d, *J* 7, 6 H, $CHMe_2$), 2.35 (s, 6 H, CH_3), 3.58 (sep., *J* 7, 1 H, N–CH), 7.17 (s, 1 H, ArH) and 7.18 (s, 2 H, ArH); *m/z* 262 (M^+).

4b. ν_{max}(Nujol)/cm^{-1} 3200 and 1725; δ_H 0.80 (s, 3 H, 4-CH_3, *cis* to Ph), 1.27 (s, 3 H, 4-CH_3, *trans* to Ph), 1.43 (d, *J* 7, 6 H, $CHMe_2$), 3.60 (sep., *J* 7, 1 H, N–CH), 4.70 (s, 1 H, OH), 7.12 (s, 1 H, ArH) and 7.20 (m, 3 H, ArH); *m/z* 268 (M^+).

4c. ν_{max}(Nujol)/cm^{-1} 3200 and 1720; δ_H 0.87 (s, 3 H, 4-CH_3, *cis* to Ph), 1.32 (d, *J* 7, 6 H, $CHMe_2$), 1.48 (s, 3 H, 4-CH_3, *trans* to Ph), 3.38 (sep, *J* 7, 1 H, N–CH) and 7.03–7.63 (m, 4 H, ArH); *m/z* 312 (M^+).

4d. ν_{max}(Nujol)/cm^{-1} 3240 and 1720; δ_H 0.88 (s, 3 H, 4-CH_3, *cis* to Ph), 1.38 (d, *J* 7, 6 H, $CHMe_2$), 1.52 (s, 3 H, 4-CH_3, *trans* to Ph), 2.33 (s, 3 H, CH_3), 3.72 (sep., *J* 7, 1 H, N–CH) and 7.00–7.33 (m, 4 H, ArH); *m/z* 248 (M^+).

4e. ν_{max}(Nujol)/cm^{-1} 3275 and 1730; δ_H 0.82 (s, 3 H, 4-CH_3, *cis* to Ph), 1.34 (d, *J* 7, 6 H, $CHMe_2$), 1.47 (s, 3 H, 4-CH_3, *trans* to Ph), 3.63 (sep., *J* 7, 1 H, N–CH), 4.92 (s, 1 H, OH) and 7.00–7.50 (m, 4 H, ArH); *m/z* 268 (M^+).

4f. ν_{max}(Nujol)/cm^{-1} 3225 and 1720; δ_H 0.83 (s, 3 H, 4-CH_3, *cis* to Ph), 1.36 (d, *J* 7, 6 H, $CHMe_2$), 1.47 (s, 3 H, 4-CH_3, *trans* to Ph), 3.63 (sep., *J* 7, 1 H, N–CH), 7.33 (d, *J* 9, 2 H, ArH) and 7.48 (d, J 9, 2 H, ArH); *m/z* 312 (M^+).

4g. ν_{max}(Nujol)/cm^{-1} 3280 and 1735; δ_H 0.92 (s, 3 H, 4-CH_3, *cis* to Ph), 1.38 (d, *J* 7, 6 H, $CHMe_2$), 1.55 (s, 3 H, 4-CH_3, *trans* to Ph), 2.37 (s, 3 H, CH_3), 3.70 (sep., *J* 7, 1 H, N–CH), 7.22 (d, *J* 3, 2 H, ArH) and 7.30 (d, *J* 3, 2 H, ArH); *m/z* 248 (M^+).

4h. ν_{max}(Nujol)/cm^{-1} 3330 and 1740; δ_H 1.07 (s, 3 H, 4-CH_3, *cis* to Ph), 1.36 (d, *J* 7, 6 H, $CHMe_2$), 1.58 (s, 3 H, 4-CH_3, *trans* to

* Chiralpak As, Chiralcel OD and Chiralcel OC are available from Daicel Chemical Industries Ltd., Himeji, Japan.

Ph), 3.50 (sep., *J* 7, 1 H, N–CH), 4.43 (s, 1 H, OH) and 7.10–7.83 (m, 4 H, ArH); *m/z* 268 (M^+).

4i. ν_{max}(Nujol)/cm^{-1} 3350 and 1740; δ_H 1.10 (s, 3 H, 4-CH_3, *cis* to Ph), 1.36 (d, *J* 7, 6 H, CHMe_2), 1.67 (s, 3 H, 4-CH_3 *trans* to Ph), 3.55 (sep., *J* 7 Hz, 1 H, N–CH) and 7.10–7.77 (m, 4 H, ArH); *m/z* 312 (M^+).

4j. ν_{max}(Nujol)/cm^{-1} 3300 and 1730; δ_H 0.90 (s, 3 H, 4-CH_3, *cis* to Ph), 1.38 (d, *J* 7, 6 H, CHMe_2), 1.55 (s, 3 H, 4-CH_3, *trans* to Ph), 2.42 (s, 3 H, CH_3), 3.50 (sep., *J* 7, 1 H, N–CH), 4.47 (s, 1 H, OH) and 7.00–7.67 (m, 4 H, ArH); *m/z* 248 (M^+).

4k. ν_{max}(Nujol)/cm^{-1} 3300 and 1740; δ_H 0.83 (s, 3 H, 4-CH_3, *cis* to Ph), 1.38 (d, *J* 7, 6 H, CHMe_2), 1.45 (s, 3 H, 4-CH_3, *trans* to Ph), 2.25 (s, 6 H, CH_3), 3.17 (s, 1 H, OH), 3.60 (sep., *J* 7, 1 H, N–CH), 3.17 (s, 1 H, OH) and 7.00–7.33 (m, 4 H, ArH); *m/z* 262 (M^+).

4l. ν_{max}(Nujol)/cm^{-1} 3275 and 1725; δ_H 0.83 (s, 3 H, 4-CH_3, *cis* to Ph), 1.37 (d, *J* 7, 6 H, CHMe_2), 1.47 (s, 3 H, 4-CH_3, *trans* to Ph), 2.32 (s, 6 H, CH_3), 3.03 (s, 1 H, OH), 3.43 (sep., *J* 7, 1 H, N–CH) and 6.80–7.17 (m, 4 H, ArH); *m/z* 262 (M^+).

5a. ν_{max}(Nujol)/cm^{-1} 1670 and 1630; δ_H 1.16 (d, *J* 7, 6 H, CHMe_2), 1.60 (d, *J* 7, 6 H, CHMe_2), 0.50–3.40 (m, 11 H), 3.70 (sep., *J* 7, 1 H, N–CH) and 7.13–8.13 (m, 5 H, ArH); *m/z* 274 (M^+).

5b. ν_{max}(Nujol)/cm^{-1} 1685 and 1640; δ_H 1.18 (d, *J* 7, 6 H, CHMe_2), 1.57 (d, *J* 7, 6 H, CHMe_2), 0.67–3.30 (m, 11 H), 3.70 (sep., *J* 7, 1 H, N–CH) and 7.20–8.07 (m, 4 H, ArH); *m/z* 308 (M^+).

6a. ν_{max}(Nujol)/cm^{-1} 1680 and 1630; δ_H 0.53–3.53 (m, 22 H) and 7.13–8.20 (m, 5 H, ArH); *m/z* 314 (M^+).

6b. ν_{max}(Nujol)/cm^{-1} 1660 and 1630; δ_H 0.53–3.53 (m, 22 H) and 7.13–8.20 (m, 5 H, ArH); *m/z* 348 (M^+).

8. ν_{max}(Nujol)/cm^{-1} 3350 and 1720; δ_H 1.36 (d, *J* 7, 6 H, CHMe_2), 0.63–2.70 (m, 10 H), 3.50 (sep., *J* 7, 1 H, N–CH) and 7.20–7.67 (m, 5 H, ArH); *m/z* 274 (M^+).

9. ν_{max}(Nujol)/cm^{-1} 3250 and 1740; δ_H 0.85 (s, 3 H, 4-CH_3, *cis* to Ph), 1.48 (s, 3 H, 4-CH_3, *trans* to Ph), 0.60–2.07 (m, 10 H), 3.20 (m, 1 H, –CH–), 4.63 (s, 1 H, OH) and 7.23–7.40 (m, 4 H, ArH); *m/z* 308 (M^+).

10a. ν_{max}(Nujol)/cm^{-1} 3200 and 1720; δ_H 0.67–2.67 (m, 21 H), 3.73 (s, 1 H, OH) and 7.17–7.77 (m, 5 H, ArH); *m/z* 314 (M^+).

10b. ν_{max}(Nujol)/cm^{-1} 3380 and 1740; δ_H 0.67–2.50 (m, 21 H), 4.25 (s, 1 H, OH), 7.27 (m, 4 H, ArH) and 7.42 (s, 1 H, ArH); *m/z* 348 (M^+).

Acknowledgements

Financial support from the Ministry of Education, Science and Culture, Japanese Government for the Grant-in-Aid for Scientific Research (B) No. 04453102 and technical assistance from Rikiya Matsugawa and Hiroyuki Oota are gratefully acknowledged.

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Paper 3/00146F
Received 11*th January* 1993
Accepted 1*st March* 1993