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Oxidative Rearrangement of Imines to Formamides using Sodium Perborate[1]

Pakawan Nongkunsarn and Christopher A. Ramsden*

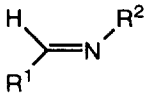
Department of Chemistry, Keele University, Keele, Staffordshire ST5 5BG, UK

Abstract: Oxidation of *C*-aryl or alkyl-*N*-arylaldimines **6** or **20** by sodium perborate tetrahydrate (SPB) in trifluoroacetic acid solution gives rearranged *N,N*-disubstituted formamides **9** and **21**. Yields are variable and solvent dependant with the best yields (50-60%) being obtained for electronically neutral *C*-aryl substituents or *C*-*s*-alkyl substituents. Product formation is rationalised in terms of an intermediate oxaziridine **5** that rearranges *via* acid catalysed O-N bond cleavage. An alternative C-O bond cleavage of these intermediates accounts for the formation of aldehydes, which are common by-products. Rearrangement appears to be favoured by *N*-aryl substituents and by *C*-substituents that do not stabilise a developing positive charge on carbon. Further support for an oxaziridine intermediate **5** is provided by the observation that MCPBA oxidation of benzaldehyde phenylimine gives rearranged *N,N*-diphenylformamide. Under the conditions of the SPB oxidative rearrangements, oxaziridine formation may well occur by initial formation of trifluoroperacetic acid. Stereochemical aspects of this novel rearrangement of aldimines **1** → **2** have been investigated using *trans*- and *cis*-myrtanal **25** and **30**. The observed epimerisation using the *N*-4-tolyl imine of *trans*-myrtanal **26** is believed to arise from equilibration of the precursor imine **26** with the tautomeric enamine **35b**.

INTRODUCTION

Sodium perborate tetrahydrate (SPB) is a cheap, stable and non-toxic oxidising agent. Over the last ten years useful oxidative transformations of a variety of organic functional groups have been achieved using this reagent. The organic chemistry of SPB up to 1994 has been reviewed.[2,3] More recently oxidations of enones,[4,5] pyruvic acids,[6] oximes,[7] organoboranes[8] and sulphides[9] have been reported. We now describe the results of our studies of the oxidative rearrangement of imines **1** of aromatic[1] and aliphatic aldehydes to formamides **2** using SPB in trifluoroacetic acid (TFA). As far as we are aware, the only previously reported examples of the direct transformation of imines to formamides are oxidations (H_2O_2/glacial AcOH) of dibenzo[*b*,*f*][1,4]oxazepines to the corresponding *N*-formylphenoxazines (0-48% yield).[10] These products were accompanied by low yields of the corresponding lactams. However, it is interesting to note that Katritzky and Eynde[11] have shown that H_2O_2-SeO_2 oxidation of the benzotriazole adducts of aldimines gives mixtures of rearranged formamides **2** and unrearranged amides **3**. Unrearranged amides **3** are also formed by oxidation of imines using either potassium permanganate in aqueous acetonitrile (50-73% yield)[12] or chromyl chloride (CrO_2Cl_2) in CCl_4 (60-75% yield).[13] The most common products of imine oxidation are (i) nitrones **4**, which are formed using either dimethyldioxirane in CH_2Cl_2/Me_2CO (39-71% yield)[14] or potassium permanganate in aqueous CH_2Cl_2 (13-89% yield),[15] and (ii) oxaziridines **5**, which are formed using peroxyacids such as peracetic acid,[16] MCPBA[14,17,18] and benzoylperoxy carbamic acid (BPC).[19] Mixtures of

nitrones **4** and oxaziridines **5** are sometimes obtained. Imines **1** are also oxidised to oxaziridines **5** (47-90% yield) by $CoCl_2$ catalysed oxidation by oxygen in the presence of an aliphatic aldehyde as a co-reductant.[20] The species **3**, **4** and **5** are therefore the expected products of imine oxidation. The unexpected formation of the rearranged formamides **2** that we now describe provides a new route to secondary amine derivatives.



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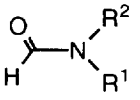

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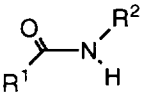

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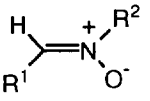

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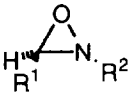

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RESULTS AND DISCUSSION

The oxidative rearrangement of the aldimines (**1**) is strongly dependant on the nature of the substituents R^1 and R^2. Accordingly, the discussion of the results is subdivided with respect to whether these substituents are aryl or alkyl. All imines were purified by recrystallisation or distillation and their purity was checked by ^1H NMR spectroscopy immediately prior to use.

C,N-*Diarylaldimines* (**6**)

Sodium perborate tetrahydrate (SPB) was added to a solution of benzaldehyde phenylimine **6a** in hot TFA (70-80 °C). A vigorous reaction was observed and the mixture was heated under reflux (1 hour). Aqueous work-up and chromatographic purification gave *N,N*-diphenylformamide **9a** (51%). In a similar manner diarylaldimines having a representative variety of simple aryl substituents were oxidised and the results are summarised in Table 1. The formamide products were fully characterised. In all cases the formamide **9** was accompanied by formation of the precursor aldehyde (Ar^1CHO). Inspection of Table 1 reveals that the yield of formamide is dependant on the nature of the aryl substituents. Although yields are modest (≤50%), the imines are readily available and this rearrangement therefore provides an attractive short route to diarylamines that may not be easily accessible by other methods.[21-23] Surprisingly, the rearrangement is inhibited by electron-rich *p*-anisyl substituents. This contrasts with other 1,2-aryl migrations, such as the Baeyer-Villiger[24] and Beckmann[25] rearrangements, in which an electron-rich substituent favours rearrangement. In a similar manner, naphthyl derivatives did not rearrange and only a complex mixture of products was obtained. In three of the reactions (aldimines **6e,l,n**) the formamide **9** was accompanied by a low yield (*ca* 10%) of the corresponding benzamide **11**. We have also investigated simple heterocyclic derivatives but no amide products **9** or **11** were detected when the pyridyl or furyl imines **6g-s** were treated with SPB: only benzaldehyde or furfuraldehyde were isolated.

All attempts to increase the yields of formamides **9** in TFA solution were unsuccessful. The reaction of benzaldehyde 4-tolylimine **6f** with SPB in TFA under various conditions was investigated. Use of excess SPB (2 or 10 equiv.) did not improve the yield nor did prolonged reaction times (2, 4 and 24 hours). At 40 °C and room temperature the yield of the formamide **9f** was reduced to 30% and 14% respectively. When glacial acetic acid was used as solvent variable results were obtained. Thus, the imine **6b** gave a slightly better yield of the formamide **9b** (32%) than in TFA solution and the *p*-anisyl derivative **6c** gave a significantly increased

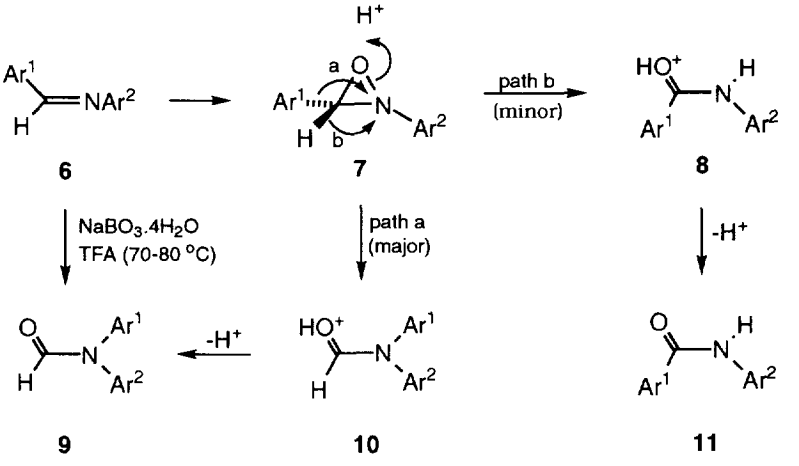
yield (18%) whereas the diphenylimine **6a** gave a much lower yield (10%). The imines **6e** and **6f** gave none of the corresponding formamides **9** and a significant yield of *N*-4-tolylbenzamide **11f** (20%) was obtained from the latter **6f**. The acidity of the solvent appears to influence the outcome of the reaction and the use of trifluoromethane sulphonic acid (TfOH) as solvent was therefore investigated. Previously, TfOH has been used in the SPB mediated electrophilic hydroxylation of arenes.[26] However, reaction of benzaldehyde 4-tolylimine **6f** with SPB in TfOH led only to a complex mixture of unidentified products with no evidence of either the formamide **9f** or the benzamide **11f** being formed.

Table 1 Oxidation of *C*, *N*-Diarylaldimines by Sodium Perborate

Entry	Ar^1	Ar^2	Aldimine (**6**) Yield(%)(mp/bp)[a]	Formamide (**9**) Yield(%)(mp)[a]
a	C_6H_5	C_6H_5	77 (49-51 °C)	51 (72 °C)
b	4-MeC_6H_4	C_6H_5	83 (42-4 °C)	20 (84-5 °C)
c	4-$MeOC_6H_4$	C_6H_5	84 (61-3 °C)	2 (oil)
d	4-ClC_6H_4	C_6H_5	86 (63-4 °C)	52 (103-4 °C)
e	4-$CF_3C_6H_4$	C_6H_5	70 (78 °C)	32 (oil)
f	C_6H_5	4-MeC_6H_4	81 (30-2 °C)	54 (84-5 °C)
g	C_6H_5	4-$MeOC_6H_4$	77 (69-70 °C)	0
h	C_6H_5	4-ClC_6H_4	73 (57-9 °C)	53 (103-4 °C)
i	C_6H_5	4-$CF_3C_6H_4$	82 (64-5 °C)	28 (oil)
j	C_6H_5	4-IC_6H_4	57 (80-1 °C)	0
k	4-ClC_6H_4	4-MeC_6H_4	92 (125-6 °C)	38 (121-2 °C)
l	3-ClC_6H_4	4-MeC_6H_4	82 (53-5 °C)	11 (84-5 °C)
m	2-ClC_6H_4	4-MeC_6H_4	78 (52-5 °C)	42 (oil)
n	2,6-$Cl_2C_6H_3$	4-MeC_6H_4	58 (34-6 °C)	8 (89-91 °C)
o	2-naphthyl	4-MeC_6H_4	82 (116-8 °C)	0
p	4-MeC_6H_4	1-naphthyl	88 (76-7 °C)	0
q	C_6H_5	2-pyridyl	79 (121-5 °C @ 0.25 mmHg)	0
r	C_6H_5	3-pyridyl	84 (120-1 °C @ 0.03 mmHg)	0
s	2-furyl	4-MeC_6H_4	72 (163-4 °C @ 19 mmHg)	0

[a] references and data on known compounds are given in the experimental section.

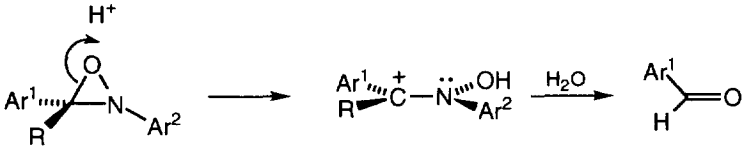
For all the imines studied variable but significant amounts of the precursor aldehydes (Ar^1CHO) were always formed. We assume that these aldehydes are formed by acid catalysed hydrolysis of an intermediate. In an attempt to inhibit this hydrolysis by removing water from the reaction medium a solution of SPB in TFA was pre-treated with trifluoroacetic anhydride (3 molar equiv.). However, subsequent reaction with the imine **6f** gave a lower yield of the formamide **9f** (38%) than by conventional treatment (54%) and use of an excess of the anhydride gave an even lower yield (10%). When the imine **6f** was treated with sodium perborate monohydrate ($NaBO_3.H_2O$) in anhydrous TFA under the standard conditions the imine remained unchanged and was isolated as its trifluoroacetate salt together with benzaldehyde, formed by hydrolysis during work-up.



Scheme 1

The formation of the formamides **9** and the benzamides **11** can be rationalised in terms of the initial formation of an intermediate *C,N*-diaryloxaziridine **7** (Scheme 1). Under protic conditions the protonated oxaziridine intermediate can undergo N-O bond cleavage with 1,2-aryl migration to the developing electron-deficient nitrogen atom leading to an *N,N*-diarylformamide **9** (pathway a). Under some circumstances 1,2-hydride shift may compete leading to formation of benzamides **11** (pathway b). In this context it is relevant to note that 1,2-hydride migration to give carboxylic acids is commonly encountered in the Dakin[27] and Baeyer-Villiger[24] oxidation of aldehydes. Formation of an intermediate oxaziridine is a reasonable proposal since oxidation of alkyl imines by peracids gives stable oxaziridines.[16-19] Diaryloxaziridines **7** are known to be much less stable and have not been isolated. Splitter and Calvin[28-30] investigated the properties of a series of *C,N*-diaryloxaziridines which were generated in solution by irradiation of isomeric nitrones **4** ($R^1=Ar^1, R^2=Ar^2$). It was found that these oxaziridines readily decomposed at room temperature to give products which included formamides **9** and benzamides **11** depending upon the solvent and substituents. In particular, under protic conditions (*e.g.* EtOH solution) formamide formation was found to be favoured whereas aprotic solvents (*e.g.* benzene) promoted formation of benzamides *via* hydride migration. These results are consistent with our observation that under the highly protic conditions of TFA solution formamide formation predominates.

It is not clear why the yield of formamide **9** is poor for aldimines bearing electron-donating substituents. It is possible that these substituents favour the alternative C-O bond cleavage of the intermediate oxaziridines (**12**; R=H) due to greater stabilisation of the developing carbocation **13** (R=H)(Scheme 2). Subsequent hydrolysis then gives the aldehyde **14** (R=H). Any nitrone formed by this route would be rapidly hydrolysed to the aldehyde **14** *via* the cation **13** under the acidic conditions of the reaction. This mechanism also rationalises our observation that ketimines do not rearrange. Treatment of either benzophenone 4-tolylimine **15** (R^1=R^2=Ph, Ar=4-MeC_6H_4) or acetophenone phenylimine **15** (R^1=Ar=Ph, R^2=Me) with SPB in TFA under the standard conditions gave only acetophenone or benzophenone respectively in high yield. We presume that for ketimines the C-O bond cleavage pathway (Scheme 2) is more favourable because the disubstituted cations **13** (R=Me,Ph) can be expected to be significantly more stable than those formed from aldimines **13** (R=H).

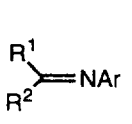


12 **13** **14**

Scheme 2

There have been few mechanistic studies of SPB oxidation and the mechanism of formation of the proposed oxaziridine intermediates **7** remains unclear. It has been suggested[2] that in acetic acid solution SPB reacts to form a peracetoxyboron ester **16** (X=H) which is the oxidising agent or that this ester hydrolyses to peracetic acid. A similar mechanism in TFA could lead to trifluoroperacetic acid (TFPA). If TFPA is the true oxidising species then the mechanism requires the presence of water to hydrolyse the peroxyborate intermediate **16** (X=F) to the peracid. We have demonstrated that anhydrous conditions employing trifluoroacetic anhydride or sodium perborate monohydrate lead to lower and zero yields respectively of the formamide: these results therefore support a mechanism in which the oxidising species is TFPA.

The possible role of TFPA as the oxidising species prompted us to investigate the oxidation of benzaldehyde phenylimine **6a** by MCPBA, which is commonly used for oxidising alkylimines to oxaziridines.[14,17,18] Treatment of the imine **6a** with MCPBA (1.2 molar equiv.) in CH_2Cl_2 solution at 0 °C did indeed give *N,N*-diphenylformamide **9a** (36%) together with benzanilide **11a** (11%) and benzaldehyde (39%). Presumably the aprotic conditions (CH_2Cl_2) lead to a significant yield of the hydride migration product **11a**.[29] As far as we are aware, the oxidation of a simple aromatic imine **6** to a formamide **9** using a peracid has not previously been reported. Since MCPBA oxidation of alkylimines to oxaziridines is well known, this observation provides additional support for the intermediacy of oxaziridines in the SPB oxidation of imines to formamides. It seems unlikely that a covalent oxaziridine precursor, *e.g.* **17**, could lead to the observed rearrangement products but we cannot eliminate the possibility that an imine-peracid complex, *e.g.* **18**,[31] leads directly to rearranged products without formation of an intermediate oxaziridine.



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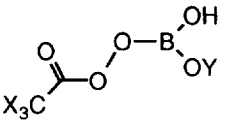

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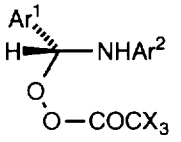

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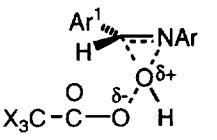

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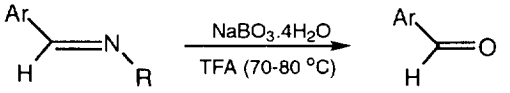
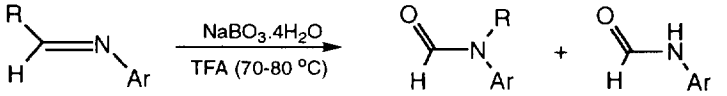
C-*Aryl*-N-*alkylaldimines* (**19**)

The aldimines **19a,b** were treated with SPB in hot TFA. Reaction appeared to be slower than with the diaryl analogues **6**: the colour of the solution changed from yellow to brown (20 mins.). No rearranged products were detected in the reaction mixture and only benzaldehyde was isolated (Equation 1). These results are consistent with previous reports[16,29] that *C*-aryl-*N*-alkyloxaziridines undergo decomposition by C-O cleavage yielding nitrones or hydrolysis products depending upon the conditions. *C*-Phenyl-*N*-*t*-butyloxaziridine, which has been prepared by irradiation of the isomeric nitrone and is relatively stable, gives benzaldehyde and *t*-butylhydroxylamine in quantitative yield when treated with aqueous methanolic sulphuric acid.[16] This mode of reaction (Equation 1) is quite different to that observed for isomeric *C*-alkyl-*N*-arylaldimines **20** (Equation 2) and possible reasons for this difference in behaviour are discussed in the following section.



(1)

19a Ar=Ph, R=^{t}Bu
19b Ar=Ph, R=PhCH$_2$



(2)

20 21 22

C-*Alkyl*-N-*arylaldimines* (**20**)

The *C*-alkyl-*N*-4-tolylaldimines **20** (Ar=4-MeC$_6$H$_4$) were prepared in good yield and their structures are fully supported by their spectral properties. Typically the cyclohexyl derivative **20c** showed a doublet at δ 7.68 corresponding to the imine proton (>CH-C*H*=N-) ; there was no evidence for the tautomeric enamine structures (>C=CH-NH-). Investigation of the SPB oxidation of these derivatives **20** (Ar=4-MeC$_6$H$_4$) demonstrated that alkyl group migration also occurs giving *N*-alkyl-*N*-arylformamides **21** (Equation 2). The results are summarised in Table 2. It is interesting to note that for this class of aldimine **20** no evidence of 1,2-hydride migration was observed and, with one exception **20a** for which a longer reaction time (5 hours) was required, no aldehyde products (RCHO) were detected. Volatile aliphatic aldehydes, however, could have been lost during reaction and work-up. In contrast to the diarylaldimines **6**, in addition to formation of the

N,N-disubstituted formamides **21** variable amounts of *N*-4-tolylformamide **22** (Ar=4-MeC_6H_4) were also isolated.

Table 2 Oxidation of *C*-Alkyl-*N*-Arylaldimines by Sodium Perborate

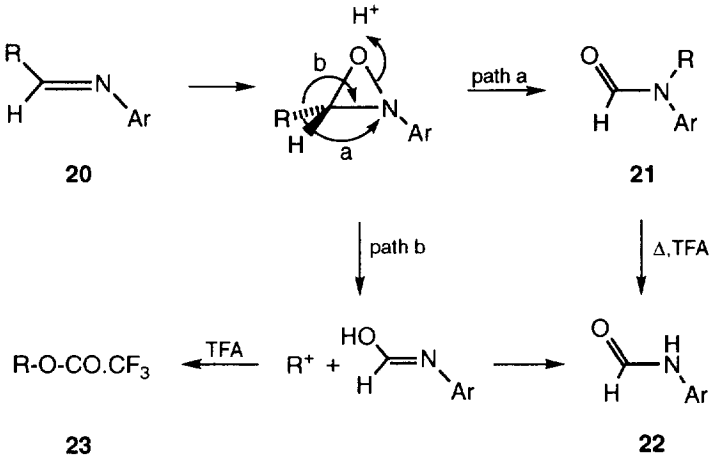
Entry	R	Ar	Aldimine (**20**) Yield(%)(bp)[a]	Formamide Products (%) (**21**)	(**22**)
a	1-adamantyl	4-MeC_6H_4	63 (79-80)[b]	5	17
b	*t*-Bu	4-MeC_6H_4	71 (77 °/ 0.08)	8	25
c	cyclohexyl	4-MeC_6H_4	67 (103-111°/ 0.28)	59	9
d	1-Me-butyl	4-MeC_6H_4	64 (90-2°/ 0.4)	53	5
e	*s* -Bu	4-MeC_6H_4	62 (90-4 °/ 0.15)	59	0
f	*i* -Pr	4-MeC_6H_4	53 (66-75 °/ 0.4)[c]	9	0

[a] °C and mmHg; [b] mp; [c] lit.[41] 100-1 °C at 3 mmHg

Two imines **20a,b** having tertiary alkyl substituents were investigated and in both cases the yield of *N,N*-disubstituted formamide **21** was low (5-8%) and this product was accompanied by a higher yield of *N*-tolylformamide **22** (Ar=4-MeC_6H_4)(17-25%). This contrasts with aldimines having a secondary alkyl substituent ,*e.g.* **22c-e**, which mainly give good yields of the *N,N*-disubstituted formamides **21** (50-60%) and low or zero yields of the *N*-arylformamide **22**.

The mechanism of formation of the *N*-tolylformamide is not clear and could occur by loss of an alkyl cation by the process shown in Scheme 3 (path b). This loss would be particularly favourable for tertiary carbocations. However, *t*-butyl is a particularly good migrating group as shown by its relative migratory aptitude in the pinacol rearrangement.[32] Furthermore, Katritzky and Eynde[11] have demonstrated that *N*-*t*-butyl-*N*-arylformamides are formed in reasonable yield by the H_2O_2-SeO_2 oxidation of benzotriazole-aldimine adducts (^{t}BuCH(Bt)NHAr). This reaction is also believed to occur by rearrangement of an intermediate oxaziridine and implies that the *t*-butyl group is a satisfactory migrating group in this rearrangement. It is interesting to note that they also detected formation of small amounts of the isomeric anilides resulting from 1,2-hydride migration. It is possible that the acidic conditions of the SPB oxidation (Equation 2) favour a competing S_N1 dissociation which would be most favourable for tertiary carbocations. Evidence for the involvement of a carbocation was provided by the observation that significant amounts of 1-adamantyl trifluoroacetate **23** (R=1-adamantyl) and 1-adamantanol were detected in the reaction mixture obtained by SPB oxidation of 1-adamantanecarboxaldehyde 4-tolylimine **20a**. Isolation of these products proved difficult. The ester hydrolysed to 1-adamantanol during chromatography and the 1-adamantanol had an identical Rf value to the formamide **21a** making complete separation of these two products difficult. However, the ester was shown to be identical by GC-MS to an authentic sample prepared from 1-adamantanol and trifluoroacetic anhydride.

An alternative mechanistic possibility is that the *N*-tolylformamide **22** is formed from the rearranged products **21** (path a) in a process analogous to the acid catalysed loss of 2-methylpropene from *t*-butylesters.[33] Support for this mechanism is provided by the observation that when the *N*-*t*-butyl-*N*-4-tolylformamide **21b** was heated in TFA at 70-80 °C (1 hour) it was quantitatively converted to *N*-4-tolylformamide **22** (Ar=4-MeC_6H_4). This process **21**→**22** could also involve the formation of an intermediate carbocation. Although we favour the latter mechanism, it is possible that both mechanisms (Scheme 3) contribute to the formation of the dealkyl products **22**.



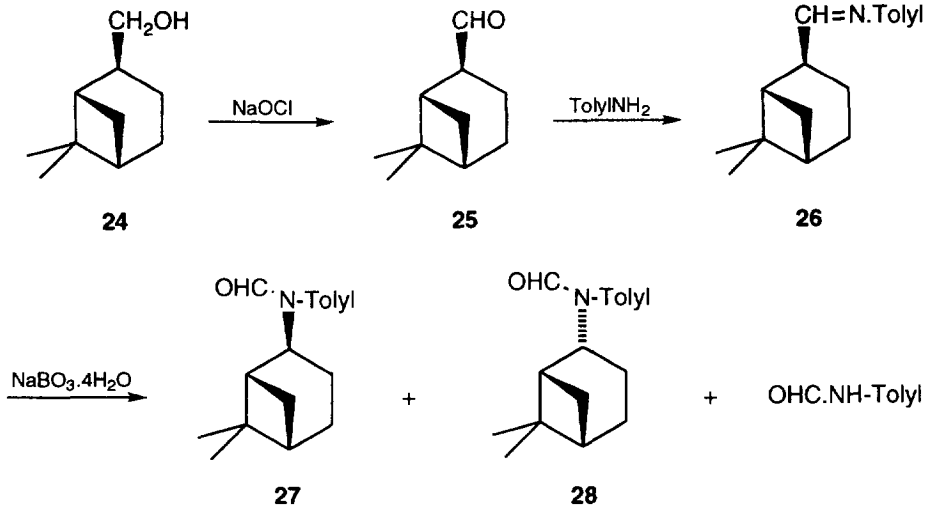
Scheme 3

Inspection of Table 2 reveals that for simple secondary alkyl substituents the yields of rearranged products are quite good. It is not clear why the yield of compound **21f** was so poor but in contrast to the other aldimines **20a-e** the precursor **20f** was particularly unstable and difficult to purify. These results for secondary alkyl derivatives are initially surprising since it is well known that aliphatic aldimines are much less stable than their aromatic analogues and the migratory aptitude of secondary alkyl groups is no better than that of aryl substituents. We suggest the following rationalisation. For the proposed *C*-alkyloxaziridine intermediates (Scheme 3) acid catalysed C-O cleavage will not be as favourable as for *C*-aryl systems since the alkyl substituents cannot stabilise the developing positive charge on carbon as effectively as an aryl group. However, the *N*-aryl substituent can stabilise the developing charge on the nitrogen atom if N-O cleavage of the oxaziridine occurs. Compared to 2,3-diaryloxaziridines **6**, therefore, N-O cleavage leading to rearrangement can be expected to compete more favourably with the undesirable C-O cleavage that leads to aldehydes. The reverse argument applies for the *C*-aryl-*N*-alkylaldimines **19** and this is consistent with our observation that only aldehyde products are obtained from these precursors.

The rationalisation described above is also consistent with our observation that SPB oxidation of the *C,C*-dialkylketimine **15** (R^1=*s*-Bu, R^2=Me, Ar=4-MeC_6H_4) gives only 3-methyl-2-pentanone (73%) and 4-toluidine (72%). In this case acid catalysed C-O cleavage of the oxaziridine leads to a secondary carbocation intermediate, which can be expected to be significantly more stable (*cf* Scheme 2) than the primary

carbocation that could form from *C*-alkylaldimines, and presumably hydrolysis of this intermediate leads to the ketone.

If the configuration of the migrating group is maintained during the reaction, the rearrangement of *C*-alkylaldimines **20** (R=alkyl) to *N*-alkyl-*N*-arylformamides **21** (R=alkyl) provides the opportunity of preparing chiral secondary amines from homochiral aliphatic aldehydes. To investigate this possibility we required a readily available and diastereomerically pure aldehyde that did not contain other sensitive functional groups. (-)-*trans*-Myrtanal **25** fulfilled these requirements being prepared by oxidation of commercial (-)-*trans*-myrtanol **24**. Furthermore, the diastereoisomer (-)-*cis*-myrtanol **29** is also available thus providing, in principle, the opportunity of preparing the epimeric aldimine **31**.



Scheme 4

trans-Myrtanal **25**[34] was obtained in 86% yield by oxidation of (-)-*trans*-myrtanol **24** using aqueous NaOCl containing a catalytic amount of tetramethylpiperidine-1-oxide (TEMPO).[35] The product was shown to be diastereomerically pure by GC and ^{1}H-NMR spectroscopy. Subsequent reaction with 4-toluidine gave a yellow liquid that was distilled under reduced pressure. The major fraction was a mixture of which the largest component was shown by GC-MS and ^{1}H-NMR to be the aldimine **26**. This material was used without further purification. All attempt to obtain a pure sample of the imine by re-distillation were unsuccessful and thermal decomposition appeared to occur. In one fraction we observed evidence that the aldimine **26** was tautomerising to the isomeric enamine **35b**. Thus, in addition to the characteristic aldimine proton at δ 7.75(d)(CH=N) and the associated methyl groups at δ 1.24(s) and 0.94(s) there were strong signals at δ 6.00(d)(=CH-N), δ 5.06(d)(NH-C) and δ 1.22(s) and 0.73(s) (>CMe$_2$) which are clearly consistent with the enamine structure **35b**. In the latter case the chemical shifts of the *gem*-dimethyl signals are very similar to those in β-pinene **35a** (δ 1.25 and 0.74)[36] whereas those in the aldimine are comparable to (-)-*trans*-myrtanal **24** (δ 1.27 and 0.89). In both cases the relative chemical shifts of the pairs of dimethyl singlets are very characteristic of the 6,6-dimethylbicyclo[3.1.1]hept-2-yl ring system.

Treatment of the crude imine **26** with SPB in TFA at 80 °C (1 hour) gave a mixture of products that contained *N*-myrtanyl-*N*-4-tolylformamide (26%) and *N*-4-tolylformamide (20%)(Scheme 4), which were separated by column chromatography. The ^{1}H-NMR spectrum of the rearranged product showed that it was a mixture of two tertiary formamides in the ratio 6:1. Although we have not been able to assign relative configurations to these products we believe that the major isomer is the expected rearrangement product **27** and that the minor product is the epimer **28**. A pure sample of the major isomer was obtained by column chromatography and the proposed structure was supported by its spectroscopic properties. The constitution of the molecular ion ($C_{17}H_{23}NO$) was confirmed by HRMS and the IR spectrum indicated the presence of a formamide carbonyl group (ν_{CO} 1681 cm^{-1}). The ^{1}H-NMR spectrum was fully consistent with the presence of *N*-2-myrtanyl and *N*-4-tolyl substituents. The proton at the 2-position of the myrtanyl group appears as a multiplet in the range δ 5.06-5.10 (CH-N<) which is consistent with the formation of a C-N bond at this position. The remainder of the myrtanyl protons show a similar pattern to those in *trans*-myrtanol **24** and *trans*-myrtanal **25** including characteristic *gem*-dimethyl singlets at δ 1.18 and 0.92. There is no evidence of rearrangement of the myrtanyl skeleton. The formamide protons appear as two singlets at δ 8.05 and δ 8.36 (5:1) due to hindered rotation about the C-N bond. Although the minor isomer could not be separated, the ^{1}H-NMR spectrum of the mixture of isomers supported the proposed tertiary formamide structure **28**. In particular, the spectrum showed the presence of two sets of formamide CH signals in the ratio 1:6. Each set appears as a discrete pair of singlets of unequal intensity giving a total of four signals at 18.5 °C (Figure 1). When the sample in d_5-nitrobenzene solution was heated these pairs of singlets independently coalesced and at 180 °C only two singlets were observed (Figure 1). For the minor component the signals coalesced at 70 °C and the signals due to the major component coalesced at 120 °C. When the sample was cooled the original pairs of singlets were restored. These observations are consistent with the proposed formamide structures **27** and **28**.

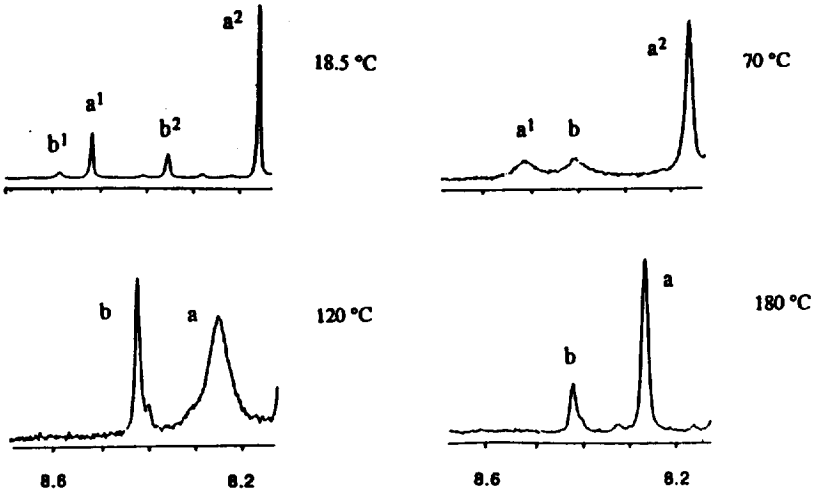
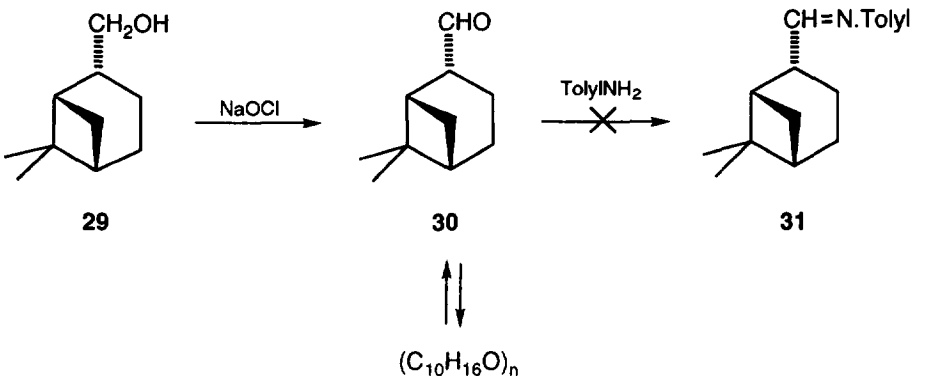
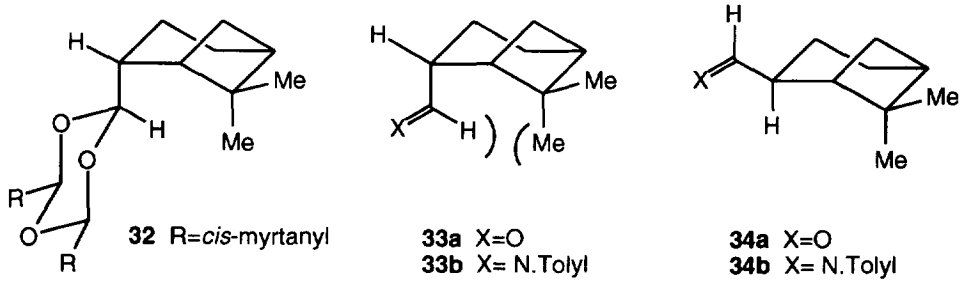


Figure 1 Temperature dependence of the ^{1}H NMR spectrum (d_5-$C_6H_5NO_2$) of a mixture of the epimers **27** and **28** showing the formamide protons of the major product (signals a) and the minor product (signals b).



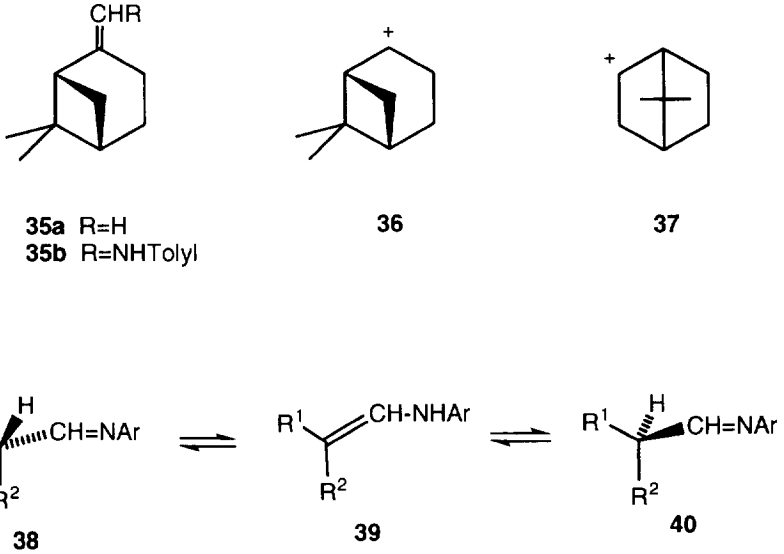
Scheme 5

The formation of the epimeric formamide **28** made it desirable to prepare and study the isomeric *cis*-aldimine **31**. *cis*-Myrtanol **29** was readily converted to the aldehyde **30** by NaOCl oxidation. This product was found to be unstable at elevated temperatures and attempts to distil it (*ca* 100 °C at 15 mmHg) resulted in rapid conversion to a colourless solid (m.p. 195-7 °C) which appears to be a polymer of the aldehyde **30**, possibly the cyclic trimer **32**. The elemental analysis of this product was consistent with the constitution $(C_{10}H_{16}O)_n$ and a carbonyl absorption was absent in the IR spectrum. The ^{1}H-NMR spectrum showed the absence of an aldehyde proton (CHO) and the observation of a doublet at δ 4.53 is consistent with the presence of an acetal proton coupled to a 2-myrtanyl proton. Characteristic 6,6-dimethyl singlets occur at δ 1.20 and 0.83. When this solid was heated under reflux in petroleum ether (b.p. 60-80 °C) in the presence of acetic acid the aldehyde **30** was regenerated. Unfortunately, all attempts to convert this aldehyde to the aldimine **31** using toluidine were unsuccessful. None of the desired product **31** was detected, even in the crude reaction mixture. We presume that the failure to form the *cis*-aldimine **31** is due to unfavourable steric interactions. It is clear from structures **33b≡31** and **34b≡26** that the *cis*-epimer **33b** can be expected to be less stable and more sterically hindered than the *trans*-isomer **34b** as a result of steric interactions between the imine function and one of the 6-methyl substituents.



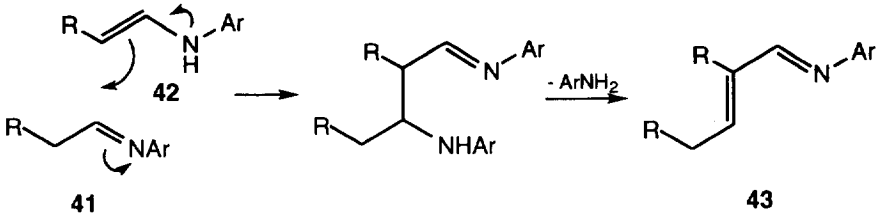
The problems associated with the stability of the 2-myrtanal 4-tolylimines **26** and **31** preclude a definitive conclusion concerning the stereochemistry of their oxidative rearrangements. The detection of the

stereoisomer **28** requires epimerisation at the 2-position of the 2-myrtanyl substituent at some stage. We believe that it is unlikely that this epimerisation occurs *via* formation of the carbocation **36**. If formed during the reaction this carbocation **36** would be expected either to be trapped by the solvent (TFA) to give the trifluoroacetate ester or to rearrange, for example, to the carbocation **37**. Analyses of the reaction mixture by GC-MS and of the isolated products by ^{1}H-NMR showed no evidence of carbocation derived products. We believe that a more probable route to the epimer **28** involves an imine-enamine tautomerisation as shown in Scheme 6. Once formed the enamine **39** can either revert to the starting imine **38** or can give the epimeric imine **40**. We have described evidence that the enamine **35b** may be formed from the aldimine **26** during its preparation and purification. Note, however, that the aldimines **20c-e** were obtained in good yield without evidence of enamine formation. In the case of the myrtanal derivatives **26** and **31** the composition of the equilibrium mixture of diastereoisomers will be influenced by the steric interactions of the bulky *gem*-dimethyl function. The *cis*-epimer **31** can be expected to be thermodynamically less stable and to form the minor component of any equilibrium mixture. Epimerisation could occur either during the preparation of the imine or under the conditions of the rearrangement.



Scheme 6

Enamine formation by the primary alkyl aldimines **41** (R=$CH_2(CH_2)_nR^1$) also accounts for the well known tendency of these derivatives to form eneimines **43**, [37] which probably arise by condensation of the enamine tautomer **42** with the aldimine (or aldehyde) precursor **41** (Scheme 7). Our attempts to isolate the imines **41** (R=Et, *n*-Pent, Ar=4-MeC_6H_4) as pure products, in order to study their SPB oxidation, gave only the eneimines **43** (R=Et, *n*-Pent, Ar=4-MeC_6H_4).



Scheme 7

C,N-*Dialkylaldimines*

We have not investigated *C,N*-dialkylaldimines, which are known to be unstable.[38,39] Our experience with *C*-aryl-*N*-alkylaldimines **19** suggests that an *N*-aryl substituent is essential for rearrangement. Furthermore, dialkylamine derivatives are readily available using other synthetic methods.

CONCLUSIONS

The rearrangement of aldimines **1** to formamides **2** can be rationalised in terms of the formation of an intermediate oxaziridine **5**, or a related imine-peracid complex, *e.g.* **18**. An *N*-aryl substituent appears to be essential and may well facilitate the reaction by stabilising the developing positive charge during N-O cleavage of the cyclic intermediate. The alternative C-O cleavage leading to aldehydes can compete and appears to be favoured when the *C*-substituent is particularly good at stabilising a developing positive charge on the carbon atom. In the diaryl series **6** optimum yields appear to be the result of a compromise between the migrating ability of the *C*-aryl substituent (*i.e.* electron-donating substituents) and the substituents capacity to disfavour C-O bond cleavage (*i.e.* electron-withdrawing substituents). The best yields are obtained with relatively neutral aryl substituents.

Secondary alkyl substituents also rearrange in reasonably good yield. Studies of the stereochemistry of this process using 2-myrtanyl derivatives indicate that epimerisation occurs. This probably takes place by tautomerisation of the aldimine precursor to the isomeric enamine (Scheme 6). Our exploratory studies of the stereochemistry of this process were limited by the instability of the aldimine diastereoisomers **26** and **31**. This instability is at least partially attributable to adverse steric interactions. Less strained chiral aldimines that are more stable may well rearrange without racemisation and this stereochemical aspect of the oxidative rearrangement of aldimines merits further study.

Because *C*-aryl and *s*- or *t*-alkyl-*N*-arylaldimines are readily prepared from the corresponding aldehyde and primary amine, this new rearrangement provides a potentially useful route to diaryl and alkylaryl amine derivatives that may not be readily accessible using other synthetic methods.[11,21-23,40,41]

EXPERIMENTAL

General Procedures. Melting points were determined using a Reichert Kofler Block apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 881 spectrophotometer with only major absorbances being quoted. Unless otherwise stated IR spectra were measured in chloroform solution. ^{1}H NMR spectra were recorded at ambient temperatures using a Jeol GSX270 FT-NMR spectrometer with tetramethylsilane (TMS) as an internal reference, and were run in deuterated chloroform solution unless otherwise stated. Chemical shifts are quoted in parts per million and the following abbreviations are used: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. Coupling constants are quoted to the nearest 0.5 Hz. Elemental analyses were determined using a Perkin-Elmer 240 CHN Elemental Analyser. Low resolution mass spectra were recorded on an AEI MS12 Mass Spectrometer at 70 eV electron impact ionisation. Separations by column chromatography were carried out using aluminium oxide (150 mesh, Aldrich) deactivated with water to Brockmann grade IV unless otherwise stated. Flash chromatography was performed using silica gel (Janssen Chimica) 0.035 - 0.07 mm. Preparative radial (chromatotron) chromatography was carried out on a Harrison Research Ltd Chromatotron 7924 using a 2 mm plate with silica gel 60 PF_{254} containing gypsum (Merck). All solvents were pre-distilled and dried appropriately prior to use. Concentration and evaporation refer to the removal of volatile materials under reduced pressure on a Büchi Rotovapor.

Preparation of *C,N*-Diarylaldimines (6)

Benzaldehyde 4-tolylimine (6f). Benzaldehyde (10.6 g, 0.1 mol) was added to a solution of 4-toluidine (10.7 g, 0.1 mol) in ethanol (50 ml). The mixture was heated under reflux (30 min) and the brown solution was then evaporated. The residual solid was recrystallised from ethanol to give compound **6f** as a yellow solid, m.p. 30-32 °C [lit.[42] 29-30 °C]; ν_{max} /cm^{-1} 2996, 1626, 1500, 1186, 1168 and 814; δ_H 2.35 (3H, s, ArC$\underline{H}_3$), 7.12 (2H, d, *J* 9 Hz, Ar$\underline{H}$), 7.17 (2H, d, *J* 9 Hz, Ar$\underline{H}$), 7.41-7.44 (3H, m, Ar$\underline{H}$) and 7.86-7.90 (2H, m, Ar$\underline{H}$) and 8.43 (1H, s, C$\underline{H}$=N); *m/z* 195 (M$^+$, 100%), 196 (35), 194 (86), 193 (16), 118 (14), 91 (41) and 65 (19).

In a similar manner the following *C,N*-diarylaldimines were prepared. Although most of these compounds have been described previously, in many cases their spectroscopic properties have not been recorded and are included here to provide full documentation of structural evidence. Benzaldehyde phenylimine **6a**, yellow solid, m.p. 49-51 °C [lit.[42] 52 °C]; ν_{max} /cm^{-1} 2998, 2880, 1186, 1168 and 688; δ_H 7.19-7.25 (3H, m, Ar$\underline{H}$), 7.35-7.49 (5H, m, Ar$\underline{H}$), 7.88-7.92 (2H, m, Ar$\underline{H}$) and 8.44 (1H, s, C$\underline{H}$=N); *m/z* 181 (M$^+$, 100%), 180 (83), 104 (12), 77 (51) and 51 (19); tolualdehyde phenylimine **6b**, yellow solid, m.p. 42-44 °C [lit.[43] b.p. 318°C/760 mmHg]; ν_{max} /cm^{-1} 2996, 1622, 1588, 1482, 1188, 1170 and 812; δ_H 2.40 (3H, s, ArC$\underline{H}_3$), 7.17-7.41 (7H, m, Ar$\underline{H}$), 7.79 (2H, d, *J* 8.5 Hz, Ar$\underline{H}$) and 8.40 (1H, s, C$\underline{H}$=N); *m/z* 195 (M$^+$, 100%), 194 (85), 91 (14), 77 (49) and 51 (19); 4-methoxybenzaldehyde phenylimine **6c**, cream solid, m.p. 61-63 °C [lit.[42] 64 °C]; ν_{max} /cm^{-1} 1604, 1586, 1572, 1508, 1250 and 1162; δ_H 3.86 (3H, s, OC$\underline{H}_3$), 6.97 (2H, d, *J* 9 Hz, Ar$\underline{H}$), 7.17-7.22 (3H, m, Ar$\underline{H}$), 7.37 (2H, t, *J* 8 Hz, Ar$\underline{H}$), 7.85 (2H, d, *J* 9 Hz, Ar$\underline{H}$) and 8.38 (1H, s, C$\underline{H}$=N); *m/z* 211 (M$^+$, 100%), 212 (21), 210 (100), 209 (19), 77 (57) and 51 (20); 4-chlorobenzaldehyde phenylimine **6d**, yellow solid, m.p. 63-64 °C [lit.[42] 64-65 °C]; ν_{max} /cm^{-1} 3002, 1624, 1588, 1488, 1086 and 724; δ_H 7.18-7.26 (3H, m, Ar$\underline{H}$), 7.38 (2H, d, *J* 8 Hz, Ar$\underline{H}$), 7.43 (2H, d, *J* 8 Hz, Ar$\underline{H}$), 7.83 (2H, d, *J* 8 Hz, Ar$\underline{H}$) and 8.40 (1H, s, C$\underline{H}$=N); *m/z* 215/217 (M$^+$, 100/32%), 216 (35), 214 (68), 77 (68) and 51 (23); 4-trifluoromethylbenzaldehyde phenylimine **6e**, colourless needles, m.p. 78 °C [lit.[44] 75-77 °C]; ν_{max} /cm^{-1} 1626,

1320, 1168, 1128, 1062 and 834; δ_H 7.22-7.44 (5H, m, ArH), 7.73 (2H, d, *J* 8 Hz, ArH), 8.02 (2H, d, *J* 8 Hz, ArH) and 8.51 (1H, s, CH=N); *m/z* 249 (M^+, 94%), 248 (66), 104 (33), 77 (100) and 51 (33); benzaldehyde 4-methoxyphenylimine **6g**, grey plates, m.p. 69-70 °C [lit.[42] 70-71 °C]; ν_{max} /cm^{-1} 3002, 1624, 1500, 1286, 1238 and 826; δ_H 3.80 (3H, s, OCH_3), 6.92 (2H, d, *J* 9 Hz, ArH), 7.23 (2H, d, *J* 9 Hz, ArH), 7.42-7.45 (3H, m, ArH), 7.86-7.90 (2H, m, ArH) and 8.38 (1H, s, CH=N); *m/z* 211 (M^+, 95%), 197 (15), 196 (100) and 167 (18); benzaldehyde 4-chlorophenylimine **6h**, cream solid, m.p. 57-59 °C [lit.[45] 56-58 °C]; ν_{max} /cm^{-1} 1626, 1576, 1482, 1186, 1166, 1086 and 826; δ_H 7.15 (2H, d, *J* 8.5 Hz, ArH), 7.35 (2H, d, *J* 8.5 Hz, ArH), 7.46-7.48 (3H, m, ArH), 7.87-7.91 (2H, m, ArH) and 8.42 (1H, s, CH=N); *m/z* 215/217 (M^+, 100/38%), 216 (41), 214 (78), 138 (14), 111 (36), 77 (16), 75 (26) and 51 (16); benzaldehyde 4-trifluoromethylphenylimine **6i**, cream powder, m.p. 64-65 °C [lit.[42] 63-65 °C]; ν_{max} /cm^{-1} 1628, 1604, 1578, 1322, 1164, 1120, 1062, 884 and 836; δ_H 7.23 (2H, d, *J* 8 Hz, ArH), 7.44-7.50 (3H, m, ArH), 7.63 (2H, d, *J* 8 Hz, ArH), 7.88-7.92 (2H, m, ArH) and 8.40 (1H, s, CH=N); *m/z* 249 (M^+, 88%), 248 (83), 230 (29), 180 (47), 152 (20), 145 (100), 125 (22), 95 (25), 77 (43), 75 (26), 69 (30), 51 (33) and 50 (24); benzaldehyde 4-iodophenylimine **6j**, grey plates, m.p. 80-81 °C [lit.[42] 82-84 °C]; ν_{max} /cm^{-1} 3004, 1624, 1574, 1476, 1188, 1168, 1002 and 818; δ_H 6.97 (2H, d, *J* 8.5 Hz, ArH), 7.47-7.49 (3H, m, ArH), 7.70 (2H, d, *J* 9 Hz, ArH), 7.87-7.91 (2H, m, ArH) and 8.42 (1H, s, CH=N); *m/z* 307 (M^+, 100%), 308 (27), 306 (68), 305 (16), 203 (16) and 76 (46); 4-chlorobenzaldehyde 4-tolylimine **6k**, colourless plates, m.p. 125-126 °C [lit.[46] 124-125 °C]; ν_{max} /cm^{-1} 2992, 1624, 1590, 1500, 1486, 1084, 884 and 824; δ_H 2.37 (3H, s, $ArCH_3$), 7.13 (2H, d, *J* 8 Hz, ArH), 7.20 (2H, d, *J* 8 Hz, ArH), 7.43 (2H, d, *J* 8.5 Hz, ArH), 7.83 (2H, d, *J* 8.5 Hz, ArH) and 8.42 (1H, s, CH=N); *m/z* 229/231 (M^+, 34/11%), 150 (26), 91 (100), 89 (65), 75 (44), 65 (90), 63 (40), 51 (34) and 39 (56); 3-chlorobenzaldehyde 4-tolylimine **6l**, yellow solid, m.p. 53-55 °C [lit.[47] 55 °C]; ν_{max} /cm^{-1} 2994, 1626, 1564, 1500, 1186 and 816; δ_H 2.37 (3H, s, $ArCH_3$), 7.14 (2H, d, *J* 8.5 Hz, ArH), 7.21 (2H, d, *J* 8.5 Hz, ArH), 7.36-7.45 (2H, m, ArH), 7.74 (1H, d, *J* 7 Hz, ArH), 7.93 (1H, t, *J* 1 Hz, ArH) and 8.42 (1H, s, CH=N); *m/z* 229/231 (M^+, 25/9%), 228 (30), 150 (30), 137 (35), 116 (38), 111 (69), 102 (51), 91 (76), 90 (60), 89 (68), 75 (80), 65 (100), 64 (45) and 62 (47); 2-chlorobenzaldehyde 4-tolylimine **6m**, brown solid, m.p. 52-55 °C [lit.[47] 52 °C]; ν_{max} /cm^{-1} 2996, 2924, 1616, 1588, 1500, 1440, 1268 and 812; δ_H 2.38 (3H, s, $ArCH_3$), 7.15-7.23 (4H, m, ArH), 7.33-7.42 (3H, m, ArH), 8.23-8.26 (1H, m, ArH) and 8.93 (1H, s, CH=N); *m/z* 229/231 (M^+, 9/3%), 102 (78), 91 (100), 89 (59), 77 (27), 76 (30), 75 (51), 65 (70), 63 (46) and 51 (48); 2,6-dichlorobenzaldehyde 4-tolylimine **6n**, light yellow crystals, m.p. 34-36 °C (Found: C, 63.49; H, 4.36; N, 5.14. $C_{14}H_{13}NO_2$ requires C, 63.66; H, 4.20; N, 5.30%); ν_{max} /cm^{-1} 2984, 1628, 1500, 1428 and 814; δ_H 2.38 (3H, s, $ArCH_3$), 7.17-7.39 (7H, m, ArH) and 8.66 (1H, s, CH=N); *m/z* 263/265/267 (M^+, 100/63/10%), 266 (15), 264 (47), 262 (52), 228 (14), 118 (27), 91 (50) and 65 (21); 2-naphthaldehyde 4-tolylimine **6o**, light yellow needles, m.p. 116-118 °C [lit.[48] 121-122 °C]; ν_{max} /cm^{-1} 2996, 1616, 1594, 1500, 858 and 820; δ_H 2.38 (3H, s, $ArCH_3$), 7.20 (4H, s, ArH), 7.50-7.54 (2H, m, ArH), 7.84-7.93 (3H, m, ArH), 8.16-8.19 (2H, m, ArH) and 8.62 (1H, s, CH=N); *m/z* 245 (M^+, 100%), 244 (87), 127 (16), 91 (25), 65 (25) and 39 (13); 4-tolualdehyde 1-naphthylimine **6p**,[49] yellow crystals, m.p. 76-77 °C; ν_{max} /cm^{-1} 3056, 3004, 1622, 1604 and 1566; δ_H 2.43 (3H, s, $ArCH_3$), 7.01-7.92 (10H, m, ArH), 8.33-8.36 (1H, m, ArH) and 8.50 (1H, s, CH=N); *m/z* 245 (M^+, 100%), 246 (19), 244 (58), 128 (14) and 127 (41); benzaldehyde 2-pyridylimine **6q**, pale yellow viscous oil, b.p. 121-125 °C/0.25 mmHg [lit.[50] 184-188 °C/18 mmHg]; ν_{max} /cm^{1} 3060, 2986, 1616, 1584, 1558, 1458, 1428, 1310, 1192, 1170, 1144 and 858; δ_H 7.15 (1H, dd, *J* 7 and 5 Hz, ArH), 7.32 (1H, d, *J* 8 Hz, ArH), 7.44-7.50 (3H, m, ArH), 7.72 (1H, dt, *J* 2

and 8 Hz, ArH), 7.97-8.01 (2H, m, ArH), 8.49 (1H, ddd, *J* 5, 2 and 0.5 Hz, ArH) and 9.15 (1H, s, CH=N); *m/z* 182 (M^+, 21%), 181 (55), 154 (8), 79 (100) and 51 (25); benzaldehyde 3-pyridylimine **6r**, pale yellow viscous oil, b.p. 120-121 °C/0.03 mmHg [lit.[51] 146-148°C/2-3 mmHg]; ν_{max} /cm^{-1} 1616, 1574, 1198, 1184, 1170, 802, 708 and 692; δ_H 7.20-7.48 (5H, m, ArH), 7.85-7.88 (2H, m, ArH), 8.44-8.48 (2H, m, ArH) and 8.36 (1H, s, CH=N); *m/z* 182 (M^+, 87%), 181 (100), 105 (9), 89 (13), 78 (49), 51 (26).

Preparation of *C,N*-Diarylketimines (15)

Benzophenone 4-tolylimine (15; R^1=R^2=Ph, Ar=4-MeC_6H_4). A mixture of benzophenone (18.2 g, 0.1 mol), 4-toluidine (21.4 g, 0.2 mol) and a few drops of hydrobromic acid (48%) in xylene (100 ml) was heated under reflux using a Dean and Stark water separator (48 h). The mixture was evaporated and distilled under diminished pressure. The bright yellow distillate solidified on standing and after recrystallisation from ethanol was identified as benzophenone 4-tolylimine (20.8 g, 77%), bright yellow crystals, m.p. 47-48 °C, b.p. 150 °C/0.2 mmHg [lit.[52] 225 °C/15 mmHg]; ν_{max} /cm^{-1} 3062, 3002, 2922, 1610, 1568, 1498, 1442, 1314, 1288, 1140, 958 and 822; δ_H 2.21 (3H, s, ArCH_3), 6.62 (2H, d, *J* 8 Hz, ArH), 6.92 (2H, d, *J* 8 Hz, ArH), 7.09-7.46 (8H, m, ArH) and 7.71-7.75 (2H, m, ArH); *m/z* 271 (M^+, 100%), 194 (84), 165 (26), 91 (39) and 65 (21).

Acetophenone phenylimine (15; R^1=Ar=Ph, R^2=Me). Acetophenone (36.0 g, 0.3 mol) was added to a solution of triethyl orthoformate (49.0 g, 0.33 mol) in ethanol (50 ml). After stirring at room temperature (24h), ethanolic sodium ethoxide was added dropwise until the pH became slightly basic (8-9). Most of the ethanol and ethylformate was then removed by distillation at atmospheric pressure. The residue was purified by distillation at 95-113 °C/20 mmHg [lit.[53] 110-120 °C/23 mmHg] to give a colourless liquid that was identified as acetophenone diethyl ketal (39.7 g, 68%). The ketal (29.1 g, 0.15 mol) was added to aniline (18.6 g, 0.20 mol) and the mixture was heated under a 6-inch Fenske ring-packed column. After distillation of ethanol was complete, the mixture was distilled under reduced pressure to obtain acetophenone phenylimine (12.9 g, 44%), as a yellow liquid, b.p. 100 °C /0.3 mmHg [lit.[54] 170 °C/15 mmHg] that gave a yellow solid, m.p. 37-38 °C [lit.[54] 37-38 °C]; ν_{max} /cm^{-1} 3064, 3000, 1636, 1592, 1480, 1364 and 1286; δ_H 2.23 (3H, s, N=CCH_3), 6.80 (2H, d, *J* 8.5 Hz, ArH), 7.05-7.47 (6H, m, ArH) and 7.96-8.00 (2H, m, ArH); *m/z* 195 (M^+, 61%), 180 (100), 118 (12), 77 (56) and 51 (20).

Preparation of *C*-Aryl-*N*-alkylaldimines (19)

Benzaldehyde *t*-butylimine (19a). A mixture of benzaldehyde (26.5 g, 0.25 mol) and *t*-butylamine (18.3 g, 0.25 mol) was stirred at 0 °C (30 min). A colourless solid formed and was removed by filtration. The liquid residue was purified by distillation under reduced pressure to give a colourless liquid that was identified as compound **19a** (14.6 g, 36%) colourless liquid, b.p. 103-107 °C/15 mmHg [lit.[55] 90-92 °C/11 mmHg]; ν_{max} (neat) /cm^{-1} 2970, 1638, 1200, 754 and 692; δ_H 1.29 (9H, s, C(CH_3)$_3$), 7.34-7.40 (3H, m, ArH), 7.72-7.76 (2H, m, ArH) and 8.26 (1H, s, CH=N); *m/z* 161 (M^+, 5%), 146, (100), 106 (24), 104 (28), 57 (55) and 41 (50).

In a similar manner benzaldehyde benzylimine **19b** (70%) was obtained as a colourless liquid, b.p. 134 °C/0.6 mmHg [lit.[17] 140 °C/1 mmHg]; ν_{max} (neat) /cm^{-1} 3030, 2846, 1640, 1024, 752 and 694; δ_H 4.79 (2H,

d, *J* 1 Hz, NC<u>H</u>$_2$), 7.20-7.41 (3H, m, Ar<u>H</u>) and 7.75-7.78 (2H, m, Ar<u>H</u>) and 8.35 (1H, t, *J* 1 Hz, C<u>H</u>=N); *m/z* 195 (M^+, 20%), 194 (23), 92 (31), 91 (100) and 65 (31).

Preparation of *C*-Alkyl-*N*-arylaldimines (20)

1-Adamantanecarboxaldehyde 4-tolylimine (20a). In a dry, three-necked flask connected to a nitrogen line and a reflux condenser, pyridinium chlorochromate (19.4 g, 0.09 mol) was suspended in anhydrous dichloromethane (50 ml). 1-Adamantane methanol (10.0 g, 0.06 mol) in dichloromethane (30 ml) was added in one portion to the magnetically stirred suspension at room temperature. After 3 h, dry ether (50 ml) was added and the supernatant liquid was filtered through a short pad of florisil®. The insoluble residue (black gum) was washed with ether (3 x 20 ml) and the liquid was also passed through florisil®. The combined ether solution was evaporated to give a pale green solid which contained 1-adamantanecarboxaldehyde (8.7 g, 88%)(>90% by ^{1}H-NMR); δ_H 1.62-2.23 (15H, m, Ada<u>H</u>), 9.40 (1H, s, C<u>H</u>O); *m/z* 164 (M^+, 4%), 135 (100), 107 (11), 93 (26), 79 (34), 67 (12) and 41 (14). Without further purification this aldehyde (8.20 g, 50 mmol) was added to a solution of 4-toluidine (4.97 g, 50 mmol) in toluene (50 ml). The mixture was heated under reflux using a Dean-Stark trap. When separation of water was complete (*ca* 3h), the solution was evaporated. The residue was recrystallised from ethanol and identified as 1-adamantanecarboxaldehyde 4-tolylimine **20a** (7.72 g, 63%), colourless needles, m.p. 79-80 °C (Found: C, 85.25; H, 9.25; N, 5.32. $C_{14}H_{13}NO_2$ requires C, 85.32; H, 9.15; N, 5.53%); ν_{max} /cm^{-1} 2910, 2852, 1650, 1452 and 820; δ_H 1.72-1.77 (12H, m, AdaC<u>H</u>$_2$), 2.00-2.80 (3H, m, AdaC<u>H</u>), 2.30 (3H, s, ArC<u>H</u>$_3$), 6.88 (2H, d, *J* 8 Hz, Ar<u>H</u>), 7.09 (2H, d, *J* 8 Hz, Ar<u>H</u>) and 7.49 (1H, s, C<u>H</u>=N); *m/z* 153 (M^+, 74%), 210 (98), 196 (18), 118 (45), 107 (24), 91 (100), 79 (42), 65 (50) and 41 (47).

The following imines were prepared in a similar manner and were used immediately after vacuum distillation and spectroscopic characterisation.

Trimethylacetaldehyde 4-tolylimine (20b), pale yellow liquid, b.p. 77 °C/0.08 mmHg; ν_{max} (liquid film) /cm^{-1} 2962, 2868, 1652, 1508 and 816; δ_H 1.17 (9H, s, C(C<u>H</u>$_3$)$_3$), 2.32 (3H, s, ArC<u>H</u>$_3$), 6.91 (2H, d, *J* 8 Hz, Ar<u>H</u>), 7.11 (2H, d, *J* 8 Hz, Ar<u>H</u>) and 7.68 (1H, s, C<u>H</u>=N); *m/z* 175 (M^+, 29%), 160 (32), 118 (100), 91 (61), 65 (24).

Cyclohexanecarboxaldehyde 4-tolylimine (20c), pale yellow liquid, b.p. 103-111 °C/0.28 mmHg; ν_{max} (neat) /cm^{-1} 2926, 2854, 1646, 1502, 1448 and 814; δ_H 1.28-1.90 (10H, m, (C<u>H</u>$_2$)$_5$), 2.28-2.41 (1H, m, CyclohexylC<u>H</u>), 2.31 (3H, s, ArC<u>H</u>$_3$) 6.92 (2H, d, *J* 8 Hz, Ar<u>H</u>), 7.10 (2H, d, *J* 8 Hz, Ar<u>H</u>) and 7.68 (1H, d, *J* 5.5 Hz, C<u>H</u>=N); *m/z* 201 (M^+, 15%), 146 (57), 133 (97), 118 (42), 91 (100), 65 (53), 55 (20), 41 (53) and 39 (42).

2-Methylvaleraldehyde 4-tolylimine (20d), pale yellow liquid, b.p. 90-92 °C/0.4 mmHg; ν_{max} (liquid film) /cm^{-1} 2962, 2928, 2870, 1684, 1504, 1456 and 812; δ_H 0.95 (3H, t, *J* 7 Hz, CH$_2$C<u>H</u>$_3$), 1.17 (3H, d, *J* 7 Hz, CHC<u>H</u>$_3$), 1.33-1.67 (4H, m, C<u>H</u>$_2$C<u>H</u>$_2$), 2.34 (3H, s, ArC<u>H</u>$_3$), 2.48-2.58 (1H, m, C<u>H</u>CH=N), 6.95 (2H, d, *J* 8 Hz, Ar<u>H</u>), 7.14 (2H, d, *J* 8 Hz, Ar<u>H</u>) and 7.67 (1H, d, *J* 6 Hz, C<u>H</u>=N); *m/z* 189 (M^+, 4%), 160 (13), 147 (100), 132 (18), 91 (55), 65 (32), 41 (24) and 39 (24).

2-Methylbutyraldehyde 4-tolylimine (20e), colourless liquid, b.p. 90-94 °C/0.15 mmHg; ν_{max} (liquid film) /cm^{-1} 2964, 2930, 2874, 1648, 1502, 1450 and 818; δ_H 0.97 (3H, t, *J* 7 Hz, CH_2CH_3), 1.15 (3H, d, *J* 7 Hz, $CHCH_3$), 1.41-1.56 (1H, m, $CH_AH_BCH_3$), 1.57-1.72 (1H, m, $CH_AH_BCH_3$), 2.32 (3H, s, $ArCH_3$), 2.37-2.47 (1H, m, CHCH=N), 6.93 (2H, d, *J* 8.5 Hz, ArH), 7.11 (2H, d, *J* 8.5 Hz, ArH) and 7.66 (1H, d, *J* 6 Hz, CH=N); *m/z* 175 (M^+, 14%), 160 (35), 147 (58), 133 (47), 118 (74), 91 (100), 65 (64) and 41 (26).

2-Methylpropionaldehyde 4-tolylimine (20f), colourless liquid, b.p. 66-75 °C/0.4 mmHg [lit.[56] 100-101 °C/3 mmHg]; ν_{max} (liquid film) /cm^{-1} 2966, 2928, 2870, 1652, 1618, 1506, 1466 and 810; δ_H 1.19 (6H, d, *J* 7 Hz, CH $(CH_3)_2$), 2.34 (3H, s, $ArCH_3$), 2.59-2.66 (1H, m, CHCH=N), 6.94 (2H, d, *J* 8 Hz, ArH), 7.13 (2H, d, *J* 8 Hz, ArH) and 7.71 (1H, d, *J* 5 Hz, CH=N); *m/z* 161 (M^+, 26%), 146 (26), 118 (100), 91 (84), 65 (42) and 39 (24).

(1*S*, 2*S*, 5*S*)-6,6-Dimethylbicyclo[3.1.1]heptane-2-carboxaldehyde 4-tolylimine (26). A mixture of (1*S*, 2*S*, 5*S*)-myrtanol (**24**) (10 g, 0.065 mol) and tetramethylpiperidine-1-oxyl (0.1012 g, 0.65 mmol, 1 mol%) in dichloromethane (25 ml) was stirred vigorously with a solution of potassium bromide (0.77 g, 6.49 mmol, 10 mol%) in water (3 ml) at -10 °C (salted ice bath). Aqueous sodium hypochlorite (120 ml, 0.5978 M, 0.0714 mol), which had been adjusted to pH 9.5 by $NaHCO_3$ immediately prior to use, was added *via* a pressure-equalising dropping funnel. The rate of addition was as fast as possible (20 min) without the reaction temperature becoming higher than 15 °C. After the addition was complete, the mixture was stirred for a further 5 min after which GC-monitoring showed complete conversion of the alcohol **24**. The organic phase was separated and the aqueous phase was extracted with dichloromethane (2x10 ml). The pale orange organic solutions were combined and washed with 10% aqueous hydrochloric acid (20 ml) containing potassium iodide (0.2 g, 1.3 mmol). The yellow solution was then washed with 10% aqueous sodium thiosulphate (10 ml) and water (10 ml). The resulting pale orange solution was finally washed with 10% aqueous $NaHCO_3$ (10 ml) and water several times until the aqueous phase was neutral. The organic phase was dried ($MgSO_4$), filtered and distilled at atmospheric pressure to remove the solvent. Distillation of the orange liquid residue under reduced pressure afforded *trans*-myrtanal **25** (8.41 g, 85.6%), colourless liquid, b.p. 94-95 °C/15-20 mmHg; ν_{max} /cm^{-1} 2926, 2871, 2806, 2711, 1729, 1464, 1385 and 1369; δ_H 0.89 (3H, s), 1.27 (1H, d, *J* 10 Hz), 1.27 (3H, s), 1.50-1.60 (1H, m), 1.80-1.87 (3H, m), 2.00-2.19 (2H, m), 2.21-2.23 (1H, m), 2.79 (1H, t, *J* 8.5 Hz) and 9.61 (1H, s, C*H*O) [lit.[34] δ_H 0.87 (3H, s), 1.03 (1H, d), 1.24 (3H, s), 1.56 (1H, m), 1.86 (2H, m), 2.08 (2H, m), 2.23 (1H, m), 2.64 (1H, s), 2.77 (1H, t) and 9.55 (1H, s)]; *m/z* 152 (M^+), 137, 123, 82, 81, 69, 67, 55, 41 (100%) and 39. A mixture of this aldehyde **25** (6.08 g, 0.04 mol) and 4-toluidine (4.28 g, 0.04 mol) in toluene (50 ml) was heated under reflux using a Dean and Stark water separator (4 h). Toluene was removed by distillation and the yellow liquid residue was subjected to distillation under reduced pressure. A major distillate (5.40 g) (b.p. 140-150 °C/0.4 mmHg) was collected and was shown by GC-MS to contain several products including the desired imine **26** (45%);*m/z* 241 (M^+), 172 (100%), 159, 118, 91, 65 and 41. Attempts to further purify this imine by redistillation were unsuccessful due to thermal decomposition. The crude imine **26** was therefore used without further purification.

Attempted Preparation of (1*S*, 2*R*, 5*S*)-6,6-Dimethylbicyclo[3.1.1]heptane-2-carboxaldehyde 4-tolylimine (33b). The oxidation of (1*S*, 2*R*, 5*S*)-myrtanol **29** (10 g, 0.0649 mol)

using sodium hypochlorite, tetramethylpiperidine-1-oxyl and potassium bromide was carried out under identical conditions to that described for (1*S*, 2*S*, 5*S*)-myrtanol **24**. After the solvent was removed, the product mixture (9.17 g, 93%) was analysed by GC-MS and shown to contain *cis*-myrtanal **30** (90%); δ_H 0.71 (3H, s), 1.21 (3H, s), 1.26 (1H, d, *J* 10 Hz), 1.45-1.72 (2H, m), 1.76-1.83 (3H, m), 1.96-2.11 (2H, m), 2.16-2.28 (1H, m), 4.53 (1H, d, *J* 7 Hz); δ_C 13.17, 23.06, 24.53, 26.68, 29.30, 38.82, 40.57, 42.26, 52.62 and 205.71; *m/z* 152 (M^+), 137, 123, 82, 81, 69, 67, 55, 41 (100%) and 39. During attempts to purify this product **30** by distillation (*ca* 100 °C/15-20 mmHg), the liquid aldehyde **30** was converted to a colourless solid that appears to be the trimer **32**, m.p. 195-197 °C (Found: C, 79.27; H, 10.88. $(C_{10}H_{16}O)_n$ requires C, 78.89; H, 10.59%); ν_{max} /cm^{-1} 2918, 2870, 1460, 1384, 1368, 1342, 1174, 1124 and 1084; δ_H 0.83 (3H, s), 1.20 (3H, s), 1.41 (1H, d, *J* 10 Hz), 1.88-1.94 (4H, m), 2.21-2.44 (2H, m), 2.52-2.57 (1H, m), 2.71-2.78 (1H, m) and 9.77 (1H, s, C<u>H</u>O); δ_C 15.94, 20.25, 23.84, 24.02, 26.68, 39.11, 39.40, 40.52, 40.73 and 104.45; *m/z* 305 (2%), 153 (34), 152 (36), 135 (100), 69 (65), 67 (51), 55 (42) and 41 (51). All attempts to prepare the desired aldimine **33b** from either the aldehyde **30** or the trimer **32** were unsuccessful.

Preparation of *C*-Alkyl-*N*-arylketimines (15)

3-Methyl-2-pentanone 4-tolylimine (15; R^1=*s*-Bu, R^2=Me, Ar=4-MeC$_6$H$_4$). 3-Methyl-2-pentanone (5.0 g, 50 mmol) was added to a solution of 4-toluidine (7.95 g, 75 mmol) in toluene (50 ml). The mixture was heated under reflux with a water separator. After 48 h, the solution was evaporated and the liquid residue was distilled under reduced pressure to give 3-methyl-2-pentanone 4-tolylimine (3.08 g, 33%), yellow liquid, b.p. 93 °C/0.65 mmHg; ν_{max} (neat) /cm^{-1} 2966, 2932, 2847, 1652 and 1504; δ_H 0.97 (3H, t, *J* 7.5 Hz, $CH_2C\underline{H}_3$), 1.17 (3H, d, *J* 7 Hz, $CHC\underline{H}_3$), 1.42-1.55 (1H, m, $C\underline{H}_AH_BCH_3$), 1.65-1.80 (1H, m, $CH_A\underline{H}_BCH_3$), 1.70 (3H, s, $C\underline{H}_3C$=N), 2.30 (3H, s, Ar$C\underline{H}_3$), 2.39-2.47 (1H, m, C<u>H</u>C=N), 6.57 (2H, d, *J* 8.5 Hz, Ar<u>H</u>) and 7.08 (2H, d, *J* 8.5 Hz, Ar<u>H</u>); *m/z* 189 (M^+, 16%), 174 (18), 161 (24), 132 (100), 91 (53), 65 (32), 41 (12) and 39 (14).

Sodium Perborate Tetrahydrate Oxidation of *N,C*-Diarylaldimines (6) in TFA.

Formation of *N*-phenyl-*N*-4-tolylformamide (9f). $NaBO_3.4H_2O$ (0.55 g, 3.6 mmol) was added to a solution of the imine **6f** (0.58 g, 3 mmol) in TFA (20 ml) at 70-80 °C. After heating under reflux (1h), the brown solution was evaporated and water (30 ml) was added. The aqueous mixture was extracted with chloroform (3x50 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to give a dark oily residue which was purified by flash chromatography (eluent: CH_2Cl_2). The major component was recrystallised from ethanol and identified as *N*-phenyl-*N*-4-tolylformamide **9f** (0.34 g, 54%), colourless solid, m.p. 84-85 °C [lit.[42b] 86-87 °C] (Found : C, 79.57; H, 6.17; N, 6.46. Calc. for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63%); ν_{max} /cm^{-1} 3004, 1674, 1490, 1336 and 1268; δ_H 2.35 and 2.37 (3H, pair of s, Ar$C\underline{H}_3$), 7.05-7.42 (9H, m, Ar<u>H</u>), 8.62 and 8.67 (1H, pair of s, C<u>H</u>O); *m/z* 211 (M^+, 100%), 212 (15), 183 (69), 182 (54), 167 (26) and 91 (20).

In a similar manner the following amides **9** and **11** were obtained from the corresponding imines (**6**) in the experiments summarised in Table 1.

***N,N*-Diphenylformamide (9a)**(51%), colourless solid, m.p. 72 °C [lit.[58] 73-74 °C] (Found: C, 79.28; H, 5.62; N, 7.02. Calc. for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10%); ν_{max} /cm^{-1} 3006, 1670, 1592, 1490,

1340 and 1268; δ_H 7.16-7.44 (10H, m, ArH), 8.68 (1H, s, CHO); *m/z* 197 (M^+, 100%), 169 (98), 168 (87), 167 (65), 77 (44), 66 (53) and 51 (57).

***N*-4-Methoxyphenyl-*N*-phenylformamide (9c)**(2%), brown oil (Found: C, 74.19; H, 5.85; N, 6.00. $C_{14}H_{13}NO_2$ requires C, 73.99; H, 5.77; N, 6.16%); ν_{max} /cm^{-1} 3004, 1674, 1592, 1500, 1492 and 1242; δ_H 3.80 and 3.82 (3H, pair of s, OCH_3), 6.90-7.44 (9H, m, ArH), 8.57 and 8.67 (1H, pair of s, CHO); *m/z* 227 (M^+, 100%), 228 (16), 199 (27), 184 (85) and 154 (16).

***N*-4-Chlorophenyl-*N*-phenylformamide (9d)**(52%), beige needles, m.p. 103-104 °C (Found: C, 67.66; H, 4.30; N, 5.95. $C_{13}H_{10}ClNO$ requires C, 67.39; H, 4.35; N, 6.05%); ν_{max} /cm^{-1} 1676, 1592, 1488, 1324, 1274, 1092 and 828; δ_H 7.09-7.45 (9H, m, ArH), 8.64 (1H, s, CHO); *m/z*. 231/233 (M^+, 70/24%), 203/205 (69/27), 168 (55), 167 (100) and 77 (44).

***N*-Phenyl-*N*-trifluoromethylphenylformamide (9e)**(32%), brown oil (Found: C, 63.49; H, 3.71; N, 5.26. $C_{14}H_{10}F_3NO$ requires C, 63.39; H, 3.80; N, 5.28%); ν_{max} /cm^{-1} 1678, 1610, 1322, 1264, 1168, 1128 and 1064; δ_H 7.18-7.67 (9H, m, ArH), 8.65 and 8.77 (1H, pair of s, CHO); *m/z* 265 (M^+, 100%), 266 (16), 237 (97), 236 (29), 168 (21), 167 (51) and 66 (25).

***N*-4-Chlorophenyl-*N*-4-tolylformamide (9k)**(38%), beige solid, m.p. 121-122 °C (Found: C, 68.63; H, 4.62; N, 5.62. $C_{14}H_{12}ClNO$ requires C, 68.43; H, 4.92; N, 5.70%); ν_{max} /cm^{-1} 1676, 1488, 1324, 1272 and 724; δ_H 2.35 and 2.38 (3H, pair of s, $ArCH_3$), 7.03-7.38 (8H, m, ArH), 8.58 and 8.63 (1H, pair of s, CHO); *m/z* 245/247 (M^+, 100/33%), 217 (53), 216 (34) and 182 (33).

***N*-3-Chlorophenyl-*N*-4-tolylformamide (9l)**(11%), pale red solid, m.p. 84-85 °C (Found: C, 68.49; H, 5.08; N, 5.47. $C_{14}H_{12}ClNO$ requires C, 68.43; H, 4.92; N, 5.70%); ν_{max} /cm^{-1} 1676, 1588, 1472, 1322 and 720; δ_H 2.37 and 2.39 (3H, pair of s, $ArCH_3$), 7.04-7.32 (8H, m, ArH), 8.57 and 8.67 (1H, pair of s, CHO); *m/z* 245/247 (M^+, 98/33%), 217/219 (81/25), 181 (85), 91 (80), 75 (100) and 63 (55).

***N*-2-Chlorophenyl-*N*-4-tolylformamide (9m)**(42%), brown oil (Found: C, 68.69; H, 4.99; N, 5.51. $C_{14}H_{12}ClNO$ requires C, 68.43; H, 4.92; N, 5.70%); ν_{max} /cm^{-1} 1676, 1508, 1476, 1330, 1274 and 724; δ_H 2.32 and 2.36 (3H, pair of s, $ArCH_3$), 7.02-7.55 (8H, m, ArH), 8.41 and 8.70 (1H, pair of s, CHO); *m/z* 245/247 (M^+, 73/26%), 217/219 (48/17), 216 (36), 210 (100), 182 (37), 180 (39), 167 (49) and 91 (35).

***N*-2,6-Dichlorophenyl-*N*-4-tolylformamide (9n)**(8%), beige solid, m.p. 90-91 °C (Found: C, 60.25; H, 3.86; N, 4.93. $C_{14}H_{11}Cl_2NO$ requires C, 60.02; H, 3.96; N, 5.00%); ν_{max} /cm^{-1} 1684, 1562, 1508, 1434, 1268, 720 and 662; δ_H 2.32 and 2.35 (3H, pair of s, $ArCH_3$), 7.04-7.49 (7H, m, ArH), 8.28 and 8.71 (1H, pair of s, CHO); *m/z* 279/281 (M^+, 78/48%), 251 (39), 244 (59), 181 (100) and 180 (32).

4-Trifluoromethyl-*N*-phenylbenzamide (11e), colourless solid, m.p. 204-205 °C [lit.[59] 198 °C] (Found: C, 63.21; H, 3.61; N, 5.05 Calc. for $C_{14}H_{10}F_3NO$: C, 63.39; H, 3.80; N, 5.28%); ν_{max} (KBr) /cm^{-1} 3350, 1656, 1530, 1324, 1170, 1114, 1066 and 954; δ_H ($CDCl_3/CD_3OD$), 7.17 (1H, t, *J* 7.5 Hz, ArH), 7.38

(2H, dd, *J* 7.5 and 7.5 Hz, ArH), 7.70 (2H, d, *J* 7.5 Hz, ArH), 7.76 (2H, d, *J* 8.5 Hz, ArH), 8.07 (2H, d, *J* 8.5 Hz, ArH); *m/z* 265 (M^+, 34%), 173 (100), 145 (82), 65 (23) and 39 (20).

***N*-4-tolylbenzamide (11f)**, colourless needles, m.p. 158-159 °C.[lit.[60] 158 °C]; ν_{max} /cm^{-1} 3440, 3004, 1666, 1592, 1512 and 1314; δ_H 2.35 (3H, s, ArCH_3), 7.18 (2H, d, *J* 8 Hz, ArH), 7.87 (2H, d, *J* 8 Hz, ArH), 7.46-7.55 (5H, m, ArH), 7.74 (1H, bs, NH); *m/z* 211 (M^+), 105 (100%), 77 and 51.

3-Chloro-*N*-4-tolylbenzamide (11l), colourless needles, m.p. 122-125 °C [lit.[61] 128 °C] (Found: C, 68.37; H, 4.76; N, 5.48 Calc. for $C_{14}H_{12}ClNO$: C, 68.43; H, 4.92; N, 5.70%); ν_{max} /cm^{-1} 3434, 3002, 2928, 1664, 1510, 1314, 1206 and 804; δ_H 2.34 (3H, s, ArCH_3), 7.15-7.85 (8H, m, ArH), 7.77 (1H, bs, NH); *m/z* 245/247 (M^+), 139/141 (100), 111/113 and 75.

2,6-Dichloro-*N*-4-tolylbenzamide (11n), colourless solid, m.p. 213-214 °C [lit.[62] 222-223 °C] (Found: C, 59.73; H, 3.68; N, 4.82 Calc. for $C_{14}H_{11}Cl_2NO$: C, 60.02; H, 3.96; N, 5.00%); ν_{max} /cm^{-1} 3420, 3004, 1674, 1508, 1428, 1316 and 760; δ_H 2.35 (3H, s, ArCH_3), 7.19 (2H, d, *J* 8.5 Hz, ArH), 7.52 (2H, d, *J* 8.5 Hz, ArH), 7.29-7.39 (3H, m, ArH); *m/z* 279/281/283 (M^+), 173/175/177 (100), 145, 109 and 77.

Reaction of Benzaldehyde 4-tolylimine (6f) with Sodium Perborate in Acetic Acid. $NaBO_3.4H_2O$ (38.46 g, 250 mmol) was added portionwise to a solution of the imine **6f** (4.88 g, 25 mmol) in glacial acetic acid (20 ml) at 40-45 °C. After heating (4h), the inorganic salts were removed by filtration. The acid mixture was concentrated, water (250 ml) was added and the aqueous mixture was extracted with chloroform (3x100 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to give crude product (6.18 g) of which 1.0 g was purified by flash chromatography (chloroform). The major component was recrystallised from ethanol and identified as *N*-4-tolylbenzamide **11f** (0.20g, 20%), colourless needles, m.p. 158-159 °C.[lit.[60] 158 °C], identical with an authentic sample.

Reaction of Benzaldehyde 4-tolylimine (6f) with Sodium Perborate in Trifluoromethanesulphonic acid. $NaBO_3.4H_2O$ (0.18 g, 1.2 mmol) was added to a solution of imine **6f** (0.195 g, 1 mmol) in trifluoromethanesulphonic acid (6 ml) maintained at 100-120 °C. The colour of the solution changed immediately to black. After 1 h., water (50 ml) was added and the aqueous mixture was extracted with chloroform (3x50 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to give a dark oily crude product. Tlc and ^{1}H-NMR analysis of the mixture showed mainly benzaldehyde together with several unidentified products. No attempt was made to separate the product mixture.

Reaction of Benzaldehyde 4-tolylimine (6f) with Sodium Perborate in TFA in the Presence of Trifluoroacetic Anhydride. A mixture of $NaBO_3.4H_2O$ (0.55 g, 3.6 mmol) and trifluoroacetic anhydride (2.27 g, 10.8 mmol) in trifluoroacetic acid (10 ml) was stirred at room temperature for 30 min before it was heated to reflux (70-80 °C). A solution of imine **6f** (0.58 g, 3 mmol) in trifluoroacetic acid (10 ml) was added. The mixture was maintained at this temperature for 1 h. The brown solution was evaporated and water (30 ml) was added. The aqueous mixture was extracted with chloroform (3x50 ml) and the combined extracts were dried ($MgSO_4$), filtered, and evaporated to give a dark oily residue which was purified by flash chromatography

(dichloromethane) to give *N*-phenyl-*N*-4-tolylformamide (**9f**)(0.24 g, 38%), identical with an authentic sample.

Reaction of Benzaldehyde 4-tolylimine (6f) with Sodium Perborate Monohydrate. The reaction was carried out under a nitrogen atmosphere. Trifluoroacetic acid was distilled from phosphorus pentoxide prior to use. $NaBO_3.4H_2O$ (0.36 g, 3.6 mmol) was added in one portion to a solution of imine **6f** (0.59 g, 3 mmol) in TFA (20 ml) maintained at 80 °C. The reaction colour changed from yellow to red-brown as soon as the SPB was added and the mixture remained this colour during 1h, after which the reaction mixture was cooled. The solution was evaporated, water (30 ml) was added and extracted with chloroform (3x30 ml). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated to give a crude mixture of yellow solid and brown oil (1.58 g). The solid was isolated by filtration and was shown to be benzaldehyde 4-tolyliminium trifluoroacetate, identical to an authentic sample prepared from benzaldehyde 4-tolylimine and trifluoroacetic acid. The brown oil was shown by ^{1}H-NMR to be mainly benzaldehyde.

Reaction of Benzaldehyde phenylimine (6a) with MCPBA. A solution of MCPBA (2.07 g, 6 mmol, 50% active) in dichloromethane (15 ml) was added dropwise to a vigorously stirred solution of the imine **6a** in dichloromethane (10 ml) maintained at 0 °C. After stirring at 0 °C (2h), the reaction mixture was filtered and poured into water (20 ml). Dichloromethane (20 ml) was added and the organic layer separated. The aqueous layer was further extracted with dichloromethane (3x10 ml). The combined organic extracts were then washed with Na_2SO_3 (1 M, 20 ml) followed by $NaHCO_3$ (2 M, 25 ml), dried ($MgSO_4$) and evaporated to give a brown oil (1.19 g). GC-MS analysis of the mixture showed benzaldehyde (39%), *N*,*N*-diphenylformamide **9a** (36%) and benzanilide **11a** (11%). Purification by column chromatography afforded pure samples of the amides **9a** (0.16 g, 16%) and **11a** (0.04 g, 4%), identical to authentic samples.

Sodium Perborate Tetrahydrate Oxidation of *C*-Alkyl-*N*-arylaldimines (20).

Formation of *N*-t-Butyl-*N*-4-tolylformamide (21b). $NaBO_3.4H_2O$ (1.10 g, 7.2 mmol) was added to a solution of imine **20b** (1.05 g, 6 mmol) in trifluoroacetic acid (30 ml) at 70-80 °C. After heating under reflux (1h), the brown solution was evaporated and water (30 ml) was added. The aqueous mixture was extracted with chloroform (3x50 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to give a dark oily residue which was purified by column chromatography (ethyl acetate : petroleum ether b.p. 60-80 °C, 1:9) to give *N*-*t*-butyl-*N*-4-tolylformamide **21b** (90 mg, 8%), colourless solid (from EtOH), m.p. 55-56 °C (Found: C, 74.86; H, 9.20; N, 7.04 $C_{12}H_{17}NO$ requires C, 75.35; H, 8.96; N, 7.32%); ν_{max} /cm^{-1} 2984, 1652, 1372 and 722; δ_H 1.39 and 1.41 (9H, pair of s, C(C<u>H</u>$_3$)$_3$), 2.35 and 2.36 (3H, pair of s, ArC<u>H</u>$_3$), 6.97 and 7.01 (2H, pair of d, *J* 8.5 Hz, Ar<u>H</u>), 7.15 and 7.20 (2H, pair of d, *J* 8.5 Hz, Ar<u>H</u>), 8.16 and 8.73 (1H, pair of s, C<u>H</u>O); *m/z* 191 (M$^+$, 32%), 148 (20), 135 (100), 107 (71), 106 (57) and 91 (21) and *N*-4-tolylformamide (**22**; Ar= 4-MeC_6H_4) (210 mg, 26%), colourless needles (from EtOH), m.p. 51-52 °C [lit.[63] 53 °C] (Found: C, 71.16; H, 6.72; N, 10.53. Calc. for C_8H_9NO: C, 71.09; H, 6.71; N, 10.37%); ν_{max} /cm^{-1} 3428, 3402, 3004, 2876, 1686, 1514, 1292 and 1230; δ_H 2.31 and 2.33 (3H, pair of s, ArC<u>H</u>$_3$), 6.98 and 7.12 (2H, pair of d, *J* 8 Hz, Ar<u>H</u>), 7.15 and 7.43 (2H, pair of d, *J* 8 Hz, Ar<u>H</u>), 8.34 and 8.63 (1H, pair of d, *J* 2 and 10 Hz, C<u>H</u>O), 8.42 (1H, bd, N<u>H</u>); *m/z* 135 (M$^+$, 97%), 136 (12), 107 (52), 106 (100), 105 (11) 79 (16), 78 (12), 77 (28) 52 (12) and 51 (14).

In a similar manner the following amides were obtained from the aldimines **20** in the experiments summarised in Table 2.

***N*-(1-Adamantyl)-*N*-4-tolylformamide (21a)**(5% by GC-MS); δ_H 2.37 (3H, s, ArC<u>H</u>$_3$), 6.96 (2H, d, *J* 8 Hz, Ar<u>H</u>), 7.20 (2H, d, *J* 8 Hz, Ar<u>H</u>), 8.15 and 8.70 (1H, pair of s, C<u>H</u>O); *m/z* 269 (M^+), 135 (100%), 107, 93, 91, 79, 77 and 41.

***N*-Cyclohexyl-*N*-4-tolylformamide (21c)**(59%), colourless needles, m.p. 45-47 °C [lit.[57] 48-49 °C] (Found: C, 77.18; H, 8.64; N, 6.55. Calc. for $C_{14}H_{19}NO$: C, 77.37; H, 8.81; N, 6.45%); ν_{max} /cm^{-1} 2938, 2862, 1654, 1506 and 1296; δ_H 0.94-1.87 (10H, m, (C<u>H</u>$_2$)$_5$), 2.36 and 2.38 (3H, pair of s, ArC<u>H</u>$_3$), 3.59 and 4.39 (1H, pair of tt, *J* 12 and 4 Hz, NC<u>H</u>), 7.03 and 7.19 (2 x 2H, d, *J* 8 Hz, Ar<u>H</u>), 8.12 and 8.40 (1H, pair of s, C<u>H</u>O); *m/z* 217 (M^+, 31%), 174 (14), 135 (100), 107 (47), 106 (38) and 91 (32).

***N*-(1-Methylbutyl)-*N*-4-tolylformamide (21d)**(53%), yellow oil (Found: C, 75.79; H, 9.43; N, 6.77. $C_{13}H_{19}NO$ requires C, 76.05; H, 9.33; N, 6.82%); ν_{max} (neat) /cm^{-1} 2964, 2932, 2870, 1670, 1508, 1372, 1290 and 1110; δ_H 0.92 and 0.95 (3H, pair of t, *J* 7 Hz, CH$_2$C<u>H</u>$_3$), 1.17 and 1.23 (3H, pair of d, *J* 7 Hz, CHC<u>H</u>$_3$), 1.33-1.63 (4H, m, C<u>H</u>$_2$C<u>H</u>$_2$), 2.36 and 2.37 (3H, pair of s, ArC<u>H</u>$_3$), 3.78-3.89 and 4.59-4.72 (1H, pair of m, NC<u>H</u>), 7.03 and 7.19 (2 x 2H, d, *J* 8 Hz, Ar<u>H</u>), 8.19 and 8.34 (1H, pair of s, C<u>H</u>O); *m/z* 205 (M^+, 24%), 190 (8), 162 (71), 135 (42), 134 (100), 91 (29) and 65 (20).

***N*-(1-Methylpropyl)-*N*-4-tolylformamide (21e)**(59%), brown oil (Found: C, 75.65; H, 8.85; N, 7.22. $C_{12}H_{17}NO$ requires C, 75.35; H, 8.96; N, 7.32%); ν_{max} (neat) /cm^{-1} 2974, 2936, 2876, 1674, 1508, 1370, 1288 and 1106; δ_H 0.96 and 1.02 (3H, pair of t, *J* 7.5 Hz, CH$_2$C<u>H</u>$_3$), 1.17 and 1.23 (3H, pair of d, *J* 7 Hz, CHC<u>H</u>$_3$), 1.39-1.68 (2H, m, C<u>H</u>$_2$CH$_3$), 2.36 and 2.38 (3H, pair of s, ArC<u>H</u>$_3$), 3.67-3.79 and 4.46-4.59 (1H, pair of m, NC<u>H</u>), 7.04 (2H, d, *J* 8 Hz, Ar<u>H</u>), 7.20 (2H, d, *J* 8 Hz, Ar<u>H</u>), 8.20 and 8.34 (1H, pair of s, C<u>H</u>O); *m/z* 191 (M^+, 20%), 162 (51), 135 (37), 134 (100), 107 (32), 106 (50), 91 (34), 77 (21) and 65 (28).

***N*-Isopropyl-*N*-4-tolylformamide (21f)**(9%), brown oil (Found: M^+, 177.1154. $C_{11}H_{15}NO$ requires, *M*, 177.1154); ν_{max} (neat) /cm^{-1} 2976, 2932, 2872, 1676, 1512, 1368, 1292 and 1258; δ_H 1.17 and 1.25 (6H, pair of d, *J* 7 Hz, CH(C<u>H</u>$_3$)$_2$), 2.36 and 2.38 (3H, pair of s, ArC<u>H</u>$_3$), 4.08 and 4.81 (1H, pair of m, NC<u>H</u>), 7.04 (2H, d, *J* 8.5 Hz, Ar<u>H</u>), 7.20 (2H, d, *J* 8.5 Hz, Ar<u>H</u>), 8.14 and 8.40 (1H, pair of s, C<u>H</u>O); *m/z* 177 (M^+, 55%), 162 (21), 135 (21), 134 (97), 108 (29), 107 (58), 106 (100), 91 (45), 77 (33), 65 (38) and 41 (28).

Reaction of (1*S*, 2*S*, 5*S*)-Myrtanal 4-tolylimine (26). $NaBO_3.H_2O$ (0.87 g, 5.5 mmol) was added to a solution of the imine **26** (2.67 g, 5 mmol, *ca* 45% active) in TFA (25 ml) maintained at 80 °C. The colour of reaction mixture quickly changed from orange-brown to dark (5 min). After being heated under reflux (1 h), the solution was evaporated and water (30 ml) was added. The mixture was extracted with chloroform (3x50 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to give a dark oily residue which was purified by column chromatography (ethyl acetate : petroleum ether b.p. 60-80 °C, 1:9) to give a mixture of *N*-(*trans*)-myrtanyl-*N*-4-tolylformamide **27** and *N*-(*cis*)-myrtanyl-*N*-4-tolylformamide **28** (*ca* 6:1 by ^{1}H-NMR,

0.34 g, 26%), brown oil. Purification of the mixture by chromatotron chromatography (ethyl acetate : petroleum ether (b.p. 60-80 °C), 1:9 as eluent) afforded *N*-(*trans*)-myrtanyl-*N*-4-tolylformamide **27** (0.11g, 9%) (Found: M^+, 257.1780, $C_{17}H_{23}NO$ requires, *M*, 257.1781); ν_{max} (neat) /cm^{-1} 2959, 2948, 2920, 2871, 1681, 1511, 1463, 1378, 1317, 1311, 1288, 1262 and 823; δ_H 0.92 (3H, s), 1.18 (3H, s), 1.20 (1H, d, *J* 10 Hz), 1.55-2.1 (7H, m), 2.34 (3H, s), 5.06-5.10 (1H, m), 7.04 (2H, d *J* 8 Hz), 7.19 (2H, d, *J* 8 Hz), 8.05 and 8.36 (1H, pair of s, CHO); *m/z* 257 (M^+), 228, 159, 144, 120 (100%), 107, 91, 77, 65 and 41.

Sodium Perborate Tetrahydrate Oxidation of *C*-Alkyl-*N*-arylketimines (15) in TFA. Oxidation of 3-methyl-2-pentanone 4-tolylimine (15; R^1=*s*-Bu, R^2=Me, Ar=4-MeC_6H_4). $NaBO_3.4H_2O$ (0.57 g, 3.6 mmol) was added to a solution of the imine **15** (R^1=*s*-Bu, R^2=Me, Ar=4-MeC_6H_4)(0.567 g, 3 mmol) in TFA (20 ml) maintained at 80 °C. The colour of the reaction mixture changed slowly from yellow to brown (2h). After heating under reflux (6h), the brown solution was evaporated, water (30 ml) was added and the mixture was extracted with chloroform (3x50 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to give a dark oily residue which was purified by column chromatography (ethyl acetate : petroleum ether (b.p. 60-80 °C), 1:9 as eluent) to give 3-methyl-2-pentanone (0.22 g, 73%), identical with an authentic sample. The aqueous layer was basified ($NaHCO_3$) and extracted with chloroform (3x50 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to give 4-toluidine (0.23 g, 72%).

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REFERENCES

1. Preliminary communication: Nongkunsarn, P.; Ramsden, C.A. *Tetrahedron Lett.*, **1993**, *34*, 6773.
2. McKillop, A.; Sanderson, W.R., *Tetrahedron*, **1995**, *51*, 6145.
3. Muzart, J.; *Synthesis*, **1995**, 1325.
4. Straub, T.S.; *Tetrahedron Lett.*, **1995**, *36*, 663.
5. Lasterra-Sanchez, M.E.; Felfer, U.; Mayon, P.; Roberts, S.M.; Thornton, S.R.; Todd, C.J., *J.Chem.Soc., Perkin Trans 1*, **1996**, 343.
6. Ramsden, C.A.; Sargent, B.J.; Wallett, C.D., *Tetrahedron Lett.*, **1996**, *37*, 1901.
7. Bandgar, B.P.; Shaikh, S.I.; Iyer, S., *Synth. Commun.*, **1996**, *26*, 1163.
8. Kabalka, G.W.; Maddox, J.T.; Shoup, T.; Bowers, K.R., *Org.Synth.*, **1996**, *73*, 116: Kabalka, G.W.; Li, N-S.; Yu, S., *Tetrahedron Lett.*, **1995**, *36*, 8545.
9. Quast, H.; Witzel, M.; Peters, E-M.; Peters, K.; von Schnering, H.G., *Liebigs Ann.*, **1995**, 725.
10. Brewster, K.; Chittenden, R.A.; Harrison, J.M.; Inch, T.D.; Brown, C. *J.Chem.Soc., Perkin Trans. 1*, **1976**, 1291.
11. Katritzky, A.R.; Eynde, J-J. V. *J.Chem.Soc., Perkin Trans. 1*, **1989**, 639.
12. Larsen, J.; Jørgensen, K.A.; Christensen, D. *J.Chem.Soc., Perkin Trans. 1*, **1991**, 1187.
13. Sandhu, J.S.; Mohan, S.; Sethi, P.S., *Chemistry and Industry*, **1970**, 1297.
14. Boyd, D.R.; Coulter, P.B.; McGuckin, M.R.; Sharma, N.D.; Jennings, W.B.; Wilson, V.E. *J.Chem.Soc., Perkin Trans. 1*, **1990**, 301.

15. Christensen, D.; Jørgensen, K.A. *J.Org.Chem.*, **1989**, *54*, 126.
16. Emmons, W.D. *J. Am. Chem. Soc.*, **1956**, *78*, 6208; **1957**, *79*, 5739.
17. Pews, R.G. *J.Org.Chem.*, **1967**, *32*, 1628.
18. Aubé, J. *Tetrahedron Lett.*, **1988**, *29*, 4509.
19. Paredes, R.; Bastos, H.; Montoya, R.; Chavez, A.L.; Dolbier, Jr., W.R.; Burkholder, C.R., *Tetrahedron*, **1988**, *44*, 6821.
20. Martiny, L.; Jørgensen, K.A., *J. Chem. Soc., Perkin Trans. 1*, **1995**, 699.
21. Miller, R.D.; Lee, V.Y.; Twieg, R.J. *J.Chem.Soc., Chem. Commun.*, **1995**, 245.
22. Gorvin, J.H. *J.Chem.Soc., Perkin Trans. 1*, **1988**, 1331.
23. Lindley, J. *Tetrahedron*, **1984**, *40*, 1433.
24. Krow, G.R. In *Comprehensive Organic Synthesis, Vol. 7*; Ley, S.V. Ed.; Pergamon Press: Oxford, 1991; pp. 671-688.
25. Craig, D. In *Comprehensive Organic Synthesis, Vol. 7*; Ley, S.V. Ed.; Pergamon Press: Oxford, 1991; pp. 689-702.
26. Prakash, G.K.S.; Krass, N.; Wang, Q.; Olah, G.A. *Synlett*, **1991**, 39.
27. Lee, J.B.; Uff, B.C. *Quart.Rev.*, **1967**, *21*, 454.
28. Splitter, J.S.; Calvin, M. *J.Org.Chem.*, **1958**, *23*, 651.
29. Splitter, J.S.; Calvin, M. *J.Org.Chem.*, **1965**, *30*, 3427.
30. Johnson, A.W. *J.Org.Chem.*, **1963**, *28*, 252.
31. Dryuk, V.G., *Tetrahedron*, **1976**, *32*, 2855.
32. Stiles, M.; Mayer, R.P. *J.Amer.Chem.Soc.*, **1959**, *81*, 1497.
33. Colvin, E.W. In *Comprehensive Organic Chemistry, Vol. 2*, Sutherland, I.O. Ed.; Pergamon Press: Oxford, 1979; p. 651.
34. Peterson, P.E.; Grant, G. *J.Org.Chem.*, **1991**, *56*, 16.
35. Antelli, P.L.; Montanari, F.; Quici, S. *Organic Synthesis*, **1990**, *69*, 212.
36. Pouchert, C.J. *The Aldrich Library of NMR Spectra, 2nd Edn.*, Vol.1, p.54.
37. Kharasch, M.S.; Richlin, I.; Mayo, F.R. *J.Amer.Chem.Soc.*, **1940**, *62*, 494.
38. Emerson, W.S.; Hess, S.M.; Uhle, F.C. *J.Amer.Chem.Soc.*, **1941**, *63*, 872.
39. Campbell, K.N.; Sommers, A.H.; Campbell, B.K. *J.Amer.Chem.Soc.*, **1944**, *66*, 82.
40. Katritzky, A.R.; Rachwal, S.; Rachwal, B. *J.Chem.Soc.Perkin Trans. 1*, **1987**, 805.
41. Katritzky, A.R.; Najzarek, Z.; Dega-Szafran, Z. *Synthesis*, **1989**, 66.
42. Roe, A.; Montgomery, J. A. *J. Am. Chem. Soc.*, **1953**, *75*, 910.
43. Law, H. D. *J. Chem. Soc.*, **1912**, *101*, 154.
44. Grigg, R.; Mitchell, T. R. B.;Tongpenyai, N. *Synthesis*, **1981**, 442.
45. Hantzsch, A.; Schwab, O. *Ber.*, **1901**, *34*, 822.
46. Tsuge, O.; Koga, M.; Shinkai, I. *Tetrahedron*, **1973**, *29*, 259.
47. Nakamura, M.; Komatsu, K.; Gondo, Y.; Ohta, H.; Ueda, Y. *Chem. Pharm. Bull.*, **1967**, *15*, 585;*Chem. Abstr.*, **1967**, *67*, 53450.
48. Lipczynska-Kochany, E.; Kochany, J. *J. Photochem. Photobiol., A*, **1988**, *45*, 65.
49. Smolders, R. R.; Brunin, D.; Sarton, F. *Bull. Soc. Chim. Belg.*, **1988**, *97*, 941.
50. Kripal, A.; Reiter, E. *Ber.*, **1927**, *60*, 664.

51. Perkampus, H.-H.; Behjati, B. *J. Heterocycl. Chem.*, *1974*, *11*, 511.
52. Reddelien, G. *Ber.*, **1913**, *46*, 2718.
53. Claisen, L. *Ber.*, **1907**, *40*, 3908.
54. Saunders, Jr., W. H.; Caress, E. A. *J. Am. Chem. Soc.*, **1964**, *86*, 861.
55. Krimm, H. *Ber.*, **1958**, *91*, 1057.
56. Latles, A.; Lafaille, L.; Verdier, A.; Mathis-Noel, R. *C. R. Acad. Sci., Paris, Ser. C.*, **1967**, *265*, 341.
57. Miller, T. G. *J. Org. Chem.*, **1966**, *31*, 3178.
58. Schmidt, O. *Ber.*, **1903**, *36*, 2459.
59. Yagupol'skii, L. M.; Gruz, B. E. *Ukrain. Khim. Zhur.*, **1957**, *23*, 634; *Chem. Abstr.*, **1958**, *52*, 9980.
60. *Beil.*, **12**, 3rd supplement, 2062.
61. Grammaticakis, P. *Bull. Soc. Chim. France*, 1963, 862.
62. Splies, R. G.; Lenga, R. E. *J. Chem. Eng. Data*, **1966**, *11*, 250.
63. *Beil.*, *12*, 3rd supplement, 2050.

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