Tetrahedron Vol. 44, No 22, pp 6841 to 6853, 1988
Printed in Great Britain

0040-4020/88 $3.00+.00
Pergamon Press plc

THERMAL O → C REARRANGEMENT OF N-PHENYL-ALLYLIMIDATES

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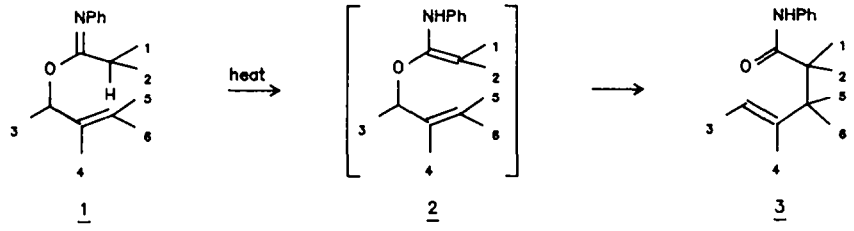
(*Received in Germany* 15 *July* 1988)

Abstract - Properly substituted N-phenyl-allylimidates 1 are shown to undergo preferential O → C sigmatropic rearrangement on heating. The diastereoselectivity of this reaction resembles the one observed in ortho ester Claisen rearrangements.

The Claisen rearrangement of allyl vinyl ether systems [1] is an exciting research subject due to the fact, that it generates the two most important functional groups in organic chemistry - the carbonyl and the olefin functionality - with the additional option of achieving high levels of stereoselectivity in the creation of sp^3 as well as sp^2 centres.
As part of a project initiated to find proper conditions for a stereocontrolled Claisen rearrangement in both a relative and absolute [2] sense using prochiral allylic alcohols, we investigated the thermal O → C rearrangement of N-phenyl-allylimidates 1:

Scheme 1



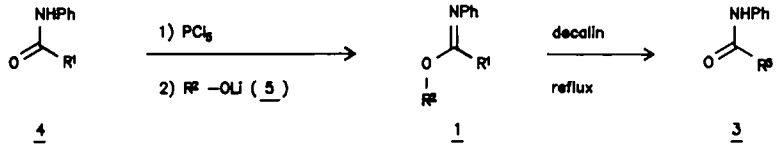
1 2 3

Heat induced O → C rearrangement of two allylimidates in which the N=C-CH fragment was incorporated in a seven-membered ring [3a], and the analogous reaction of acyclic S-allylthioimidates [3b] have already been reported. In both cases a competition between O(S) → C and O(S) → N rearrangement was possible, and it was found that C,C-coupling took place mainly [3a] to exclusively [3b]. While a highly stereoselective reaction was observed with the former substrates which can only react via an E-configured N,O-ketene acetal isomer, the question of diastereoselectivity was not addressed with the latter acyclic systems [4].

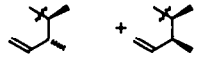
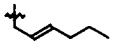
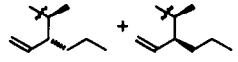
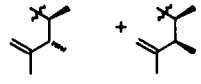
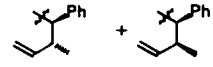
The requisite N-phenyl-allylimidates 1 are readily available from amides 4 and allylic alcohols in fair to good yields (Table 1) by conversion of 4 to an intermediate imidochloride [5] and subsequent reaction of the crude imidochloride with the lithium alkoxides 5. This procedure avoids the large excess of allylic alcohol needed for the preparation of 1 by transesterification of alkylimidates [3a,6]. N-Phenyl-allylimidates 1a - 1l are configurationally homogenous around the carbon-nitrogen double bond (^{1}H-NMR, ^{13}C-NMR, capillary GC). In analogy to N-alkyl imidates they presumably exist as E(C=N) isomers [7].

Table 1.

Preparation and Thermal O → C Rearrangement of N-Phenyl-allylimidates 1.



4 1 3

	Preparation of 1			Rearrangement of 1		
Entry	R^1	R^2	Yield 1 (%) [a]	t(h)	R^3	Yield 3 (%) [a]
a	Me		44	72		38
b	"		62	80		10 [b]
c	Et		68	24		55
d	"		63	48		(2·0:1) [c] 69
e	"		72	24		(2·0:1) [c] 65
f	"		66	72	" + "	(1:1·6) [c] 26
g	"		61	24		(3·5:1) [c] 62
h	"		73	56		20
i	"		37	67	 [d]	65
j			50	24		73
k	"		66	42		6 [b]
l			62	24		(1·6:1) [e] 93

a) Yield of purified product. b) By GC analysis of the product mixture; structure elucidated by GC/MS. c) Determined by GC. d) E : Z = 97.2 : 2.8 by GC. e) Determined by ^{1}H-NMR.

Table 1 shows the results of the thermal reaction of N-phenyl-allylimidates 1 to unsaturated amides 3.

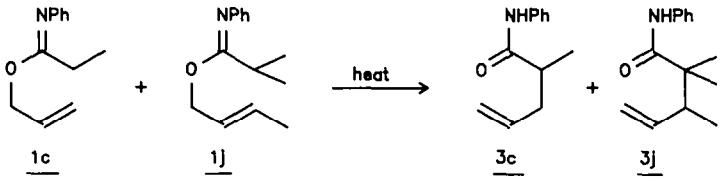
In addition to the products listed, varying amounts of precursor amides 4 and O → N allylic rearrangement products[6] were formed. While O → N rearrangement is favoured over O → C shift for imidates with R^1 = Me, all other imidates studied give predominantly (3 : 1 to 100 : 0) C,C-coupling product 3 with the exception of entry h (O → C : O → N = 1 : 1.8 by GC).

Rearrangement of the one studied imidate 1i derived from a secondary allylic alcohol demonstrates a remarkable control over the configuration of the newly formed C,C-double bond.

The yields of entries b, h, k indicate that this method is not suitable for the construction of quarternary carbon centers at C-3 of 3, whereas a quarternary center at C-2 is easily set up (entry j). Indeed, the marked increase in yield, which is observed along the line of entries a, d, j, l clearly states an increasing facility for the required isomerization process 1 → 2 (Scheme 1) in the same order.

The strong dependance of the rearrangement yields on the degree of substitution, and also the unexpected diastereoselectivity noted (vide infra), led us to anticipate that ketene imines might be involved[8] in the isomerization 1 → 2, so that the yields obtained would reflect the relative stabilities of these intermediates[9]. However, the rearrangement of an equimolar mixture of 1c and 1j either in decalin solution or neat at 200 °C gave rise to solely 3c and 3j, while no cross-over products could be detected:

Scheme 2

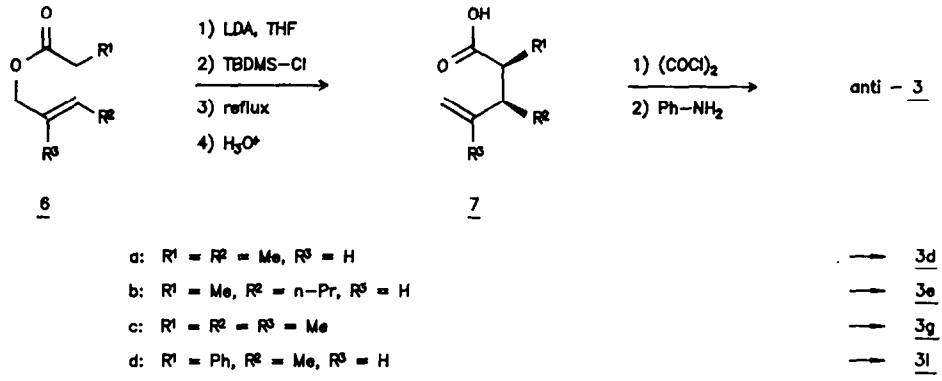


This result suggests that a different isomerization mechanism is operative, and that a high degree of substitution at C-2 in 1 might simply stabilize 2 (Scheme 1), and thus surpress competitive reactions of 1.

Rearrangement of 1d and 1g in the presence of 5 mol-% 2-hydroxypyridine, which has been advantageous for some cyclic allyl imidates[3a], did not lead to a significant change of yields or reaction times but caused a slight drop in stereoselectivity for the formation of 3d (syn-3d : anti-3d = 1.5 : 1).

The relative stereochemistry of the rearrangement products 3 in entries d, e, f, g was elucidated by comparison (capillary GC, ^{1}H-NMR) to reference substances prepared by subjecting the corresponding E-configured allyl carboxylic esters 6 to Ireland-Claisen rearrangement in THF, followed by transformation of the resulting acids 7 to anilides 3 as illustrated by Scheme 3. It is well documented that deprotonation of 6 ($R^1 \neq$ Ph) with lithium amides in THF and subsequent silylation and rearrangement produce the 2,3-anti acids 7 preferentially[10].

Scheme 3

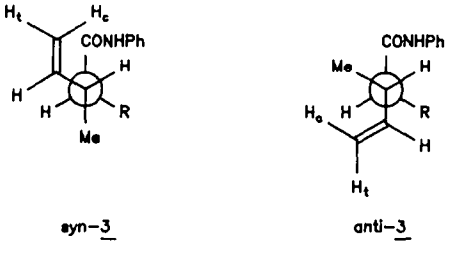


The stereochemical assignment for amides syn-3l and anti-3l is based on their ^{1}H-NMR spectral data (Table 2).

Table 2.
Chemical Shifts (ppm) of 3l and 3d.

	C-3 Me	4-H	5-H_c	5-H_t
syn-3l	0.86	5.93	5.18	5.04
anti-3l	1.20	5.57	4.91	4.86
syn-3d	1.08	5.83	5.07	5.01
anti-3d	1.08	5.71	5.10	5.08

Scheme 4



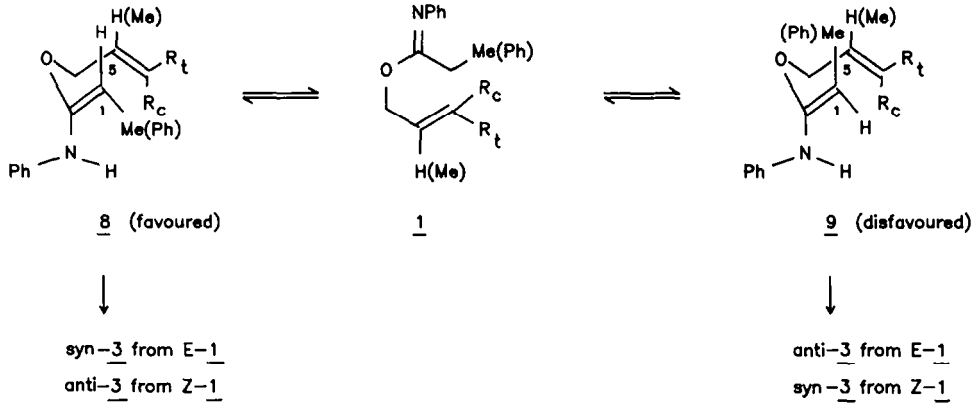
Scheme 4 shows the preferred conformations for the two isomers. Whereas there is no significant chemical shift difference for the C-3 methyl group and the vinyl protons of syn-3d and anti-3d, the anisotropy of the phenyl group in 3l causes a considerable upfield shift of the substituent gauche to it - C-3 methyl protons in syn-3l and vinyl protons in anti-3l, respectively [11].

It is interesting to note that Ireland-Claisen rearrangement of 6d follows the usual course, which implies formation of an intermediate E-silylketene acetal in THF, while analogous deprotonation and subsequent silylation of methyl phenylacetate was reported to yield a Z-silylketene acetal predominantly [10].

To exclude the possibility of concomitant thermal epimerization syn-3 ⇌ anti-3, pure isomers syn-3e and anti-3e were heated in refluxing decalin over a period of 24 h in separate experiments. In both cases the substrates proved to be configurationally stable, demonstrating that the syn/anti ratios given in Table 1 truly reflect the inherent diastereoselectivity of the rearrangement.

In contrast to reported diastereoselective Claisen rearrangements of O-allyl N,N-dialkyl N,O-ketene acetals, which predominantly yield 2,3-anti products from E-allylic alcohols and 2,3-syn products from Z-allylic alcohols if conducted under thermodynamic control [8,12,13], we observed the opposite diastereoselectivity.

Scheme 5



Scheme 5 provides a rationale for the stereoselection found. Whereas N,N-dialkyl N,O-ketene acetals cannot escape from a severe steric interaction between one alkyl group on nitrogen and a carbon substituent at C-1 in an E-ketene acetal similar to 8, thus rendering the N,N-dialkyl analogue of Z-ketene acetal 9 more favourable [12], the E-N,O-ketene acetal isomer 8 of 1 does not necessarily suffer from such an allylic strain, as depicted in Scheme 5.

With allylimidates 1 it seems to be more important that unfavourable 1,3-diaxial-like interactions between substituents at C-1 and C-5 in 9 are avoided, which become especially strong in the case of a C-5 substituent bigger than hydrogen (Table 1, entry g). The syn/anti ratios noted in this study resemble very much the values found in corresponding ortho ester Claisen rearrangements, where a similar argument was made [11].

Summarizing the synthetic aspect of this work, it is evident that good yields of thermal O → C rearrangements can be achieved with allylimidates 1, which possess C-2 substituents capable of stabilizing the isomeric N,O-ketene acetal double bond and an E-configured allylic ether moiety, while the best stereoselectivity results if a double bond substituent vicinal to the allylic oxygen is present.

Further aspects of this project are under active investigation.

Acknowledgement - This work was supported by the Deutsche Forschungsgemeinschaft.

EXPERIMENTAL

General remarks - Solvents were dried by distillation from Na (THF) or else from CaH_2. All reactions were run under Ar using flame-dried glassware. Flash chromatography was performed on silica gel 40 - 63 μm (Merck). HPLC separations were performed with a Knauer 64 pump, a Knauer differential refractometer and a 25 cm Knauer Polygosil 60 (5 μm) column, 3.2 cm i.d.. Capillary GC analyses were performed with a Shimadzu GC-9A, a Shimadzu CR3A integrator and a 25 m OV 225 CB column, 0.25 mm i.d., 0.25 μm film. Boiling points for bulb-to-bulb distillations refer to bath temperatures. Melting points were determined on a Kofler microscope-desk.
IR spectra (Shimadzu IR-408): absorption frequencies reported in cm^{-1}, solvent $CHCl_3$ unless otherwise specified. ^1H-NMR spectra (Bruker WM 300, 300 MHz) and ^{13}C-NMR spectra (Bruker WM 300, 75.47 MHz): chemical shifts in ppm relative to tetramethylsilane, solvent $CHCl_3$, ^{13}C-multiplicities were determined using INEPT pulse sequences. Mass spectra (Varian MAT CH-7A, Finnigan MAT 8230, Finnigan MAT 312; 70 eV): signals given in m/z with relative intensity (%) in brackets.
(E)-2-Butenol and (E)-2-methyl-2-butenol were prepared by $LiAlH_4$ reduction of the corresponding aldehydes [14].

Amides 4. - General procedure [15]: A 1.0 M solution of aniline in CH_2Cl_2 containing 1.1 equivalents of pyridine was cooled to 0°C. After the addition of 1.05 equivalents of the required acid chloride the cooling bath was removed and the mixture was stirred at room temp. for 16 h. The reaction mixture was washed successively with water (3x), satd. $NaHCO_3$ solution (1x), and brine (1x). The organic layer was dried over Na_2SO_4, and the solvent was removed in vacuo. Recrystallization from ligroin gave the pure amide 4. Reactions were run on a 100 - 200 mmol scale.

N-Phenylpropanamide (4c) [16]: Yield 84 %. - m.p. 104 - 106°C. - IR (KBr): 1665 (C=O), 1600 (C=C). - ^1H-NMR: 1.24 (t, J = 7.5 Hz, 3 H, CH_2-C$\underline{H}_3$), 2.39 (q, J = 7.5 Hz, 2 H, C$\underline{H}_2$-CH_3), 7.0 - 7.6 (m, 6 H, aromatic H, NH). - ^{13}C-NMR: 9.65 (CH_3), 30.52 (CH_2), 119.95 (CH), 124.03 (CH), 128.80 (CH), 138.02 (C), 172.51 (C). - MS: 149 (17) [M^+], 93 (100) [Ph-NH_2^+], 57 (36) [C_2H_5-CO^+].

N-Phenyl-2-methylpropanamide (4l) [17]: Yield 74 %. - m.p. 104 - 105°C. - IR: 1680 (C=O), 1600 (C=C). - ^1H-NMR: 1.27 [d, J = 6.9 Hz, 6 H, CH(C$\underline{H}_3$)$_2$], 2.52 [sept, J = 6.9 Hz, 1 H, C$\underline{H}$(CH$_3$)$_2$], 7.0 - 7.6 (m, 6 H, aromatic H, NH). - ^{13}C-NMR: 19.56 (CH_3), 36.70 (CH), 119.82 (CH), 124.15 (CH), 128.96 (CH), 138.06 (C), 175.22 (C). - MS (GC/MS): 163 (13) [M^+], 120 (3) [M - $CH(CH_3)_2$], 93 (98) [Ph-NH_2^+], 43 (100) [$CH(CH_3)_2^+$].

N-Phenyl-2-phenylacetamide (4l) [18]: Yield 84 %. - m.p. 112 - 114°C. - IR: 1675 (C=O), 1595 (C=C). - ^1H-NMR: 3.73 (s, 2 H, C$\underline{H}_2$-Ph), 7.0 - 7.5 (m, 11 H, aromatic H, NH). - ^{13}C-NMR: 44.88, 119.83, 124.47, 127.69, 128.94, 129.25, 129.52, 134.45, 137.62, 169.04. - MS: 211 (12) [M^+], 93 (100) [Ph-NH_2^+], 91 (95) [$C_7H_7^+$], 65 (78) [$C_5H_5^+$].

Allylimidates 1. - General procedure: The amide 4 was stirred with an equivalent amount of PCl_5 in benzene (2 ml / mmol 4) under reflux for 1 h. After cooling to room temp. benzene and the resulting $POCl_3$ were removed with the aid of a rotovapor, which was refilled with Ar after evaporation of the volatiles. The remaining crude imidochloride was dissolved in THF (1 ml / mmol 4). This solution was added dropwise by syringe to a cooled (0°C) suspension of 1.1 equivalents of the required lithium alkoxide 5 in THF [prepared by addition of an equivalent amount of 2.4 M n-BuLi in hexane to a solution of the corresponding allylic alcohol in THF (0.91 ml / mmol allylic alcohol) at 0°C and subsequent stirring for 30 min at 0°C]. The resulting reaction mixture was allowed to warm to room temp. and stirred for 20 h. After removing the solvent in vacuo the residue was taken up with CH_2Cl_2. Washing with a satd. NH_4Cl solution, followed by drying over $MgSO_4$ and evaporation of the solvent in vacuo yielded the crude allylimidate 1, which was purified by bulb-to-bulb distillation (100 - 130°C, 0.01 Torr). Reactions were run on a 10 - 15 mmol scale.

(E)-2-Butenyl N-Phenylacetimidate (1a): Yield 44 %. - IR: 1670 (C=N), 1595 (C=C). - ^{1}H-NMR: 1.76 (br. d, J = 6.2 Hz, 3 H, C=CH-C$\underline{H}_3$), 1.83 (s, 3 H, N=C-CH$_3$), 4.62 (br. d, J = 6.1 Hz, 2 H, OC$\underline{H}_2$-CH), 5.73 (qtd, J_q = 1.3 Hz, J_t = 6.2 Hz, J_d = 15.4 Hz, 1 H, CH$_2$-C$\underline{H}$=CH-CH$_3$), 5.85 (tqd, J_t = 0.8 Hz, J_q = 6.2 Hz, J_d = 15.4 Hz, 1 H, CH$_2$-CH=C$\underline{H}$-CH$_3$), 6.7 - 7.4 (m, 5 H, aromatic H). - ^{13}C-NMR: 16.13 (CH$_3$), 17.85 (CH$_3$), 66.50 (CH$_2$), 121.11 (CH), 122.80 (CH), 125.98 (CH), 128.92 (CH), 130.60 (CH), 149.11 (C), 160.82 (C). - MS: 189 (8) [M$^+$], 174 (13) [M - CH$_3$], 93 (100) [Ph-NH$_2^+$], 77 (62) [Ph$^+$], 55 (88) [CH$_3$-CH=CH-CH$_2^+$]. - Analysis: $C_{12}H_{15}NO$ (189.3) Calcd. C 76.14 H 7.99 Found C 76.39 H 7.85 .

3-Methyl-2-butenyl N-Phenylacetimidate (1b): Yield 62 %. - IR: 1660 (C=N), 1590 (C=C). - ^{1}H-NMR: 1.75 (s, 3 H, CH$_3$), 1.80 (s, 3 H, CH$_3$), 1.84 (s, 3H, CH$_3$), 4.69 (d, J = 7.1 Hz, 2 H, OC$\underline{H}_2$-CH), 5.48 (br. t, J = 7.1 Hz, 1 H, CH$_2$-C$\underline{H}$=C), 6.7 - 7.4 (m, 5 H, aromatic H). - ^{13}C-NMR: 16.08 (CH$_3$), 18.02 (CH$_3$), 25.76 (CH$_3$), 62.63 (CH$_2$), 119.45 (CH), 121.08 (CH), 122.71 (CH), 128.85 (CH), 137.94 (C), 149.17 (C), 160.98 (C). - MS: 203 (5) [M$^+$], 135 (30) [CH$_3$-CO-NHPh$^+$], 93 (100) [Ph-NH$_2^+$], 69 (29) [(CH$_3$)$_2$C=CH-CH$_2^+$]. - Analysis: $C_{13}H_{17}NO$ (203.3) Calcd. C 76.80 H 8.43 Found C 76.68 H 8.52 .

2-Propenyl N-Phenylpropanimidate (1c): Yield 68 %. - IR (film): 1670 (C=N), 1600 (C=C). - ^{1}H-NMR: 1.11 (t, J = 7.6 Hz, 3 H, CH$_2$-C$\underline{H}_3$), 2.22 (q, J = 7.6 Hz, 2 H, C$\underline{H}_2$-CH$_3$), 4.74 (d, J = 5.7 Hz, 2 H, OC$\underline{H}_2$-CH), 5.27 (br. d, J = 10.5 Hz, 1 H, CH=CH-$\underline{H}$), 5.40 (br. d, J = 17.3 Hz, 1 H, CH=CH-$\underline{H}$), 6.07 (tdd, J_t = 5.5 Hz, J_d = 10.7 Hz, J_d = 17.4 Hz, 1 H, C$\underline{H}$=CH$_2$), 6.7 - 7.4 (m, 5 H, aromatic H). - ^{13}C-NMR: 11.04 (CH$_3$), 23.26 (CH$_2$), 66.16 (CH$_2$), 117.08 (CH$_2$), 121.05 (CH), 122.67 (CH), 128.90 (CH), 133.31 (CH), 148.75 (C), 163.97 (C). - MS (GC/MS): 189 (36) [M$^+$], 174 (4) [M - CH$_3$], 160 (6) [M - C$_2$H$_5$], 133 (100) [M - CH$_2$=CH-CHO], 132 (82) [M - CH$_2$=CH-CH$_2$O], 77 (37) [Ph$^+$], 41 (39) [CH$_2$=CH-CH$_2^+$]. - Analysis: $C_{12}H_{15}NO$ (189.3) Calcd. C 76.14 H 7.99 Found C 76.17 H 7.83 .

(E)-2-Butenyl N-Phenylpropanimidate (1d): Yield 63 %. - IR (film): 1665 (C=N), 1600 (C=C). - ^{1}H-NMR: 1.08 (t, J = 7.6 Hz, 3 H, CH$_2$-C$\underline{H}_3$), 1.76 (br. d, J = 6.2 Hz, 3 H, C=CH-C$\underline{H}_3$), 2.17 (q, J = 7.6 Hz, 2 H, C$\underline{H}_2$-CH$_3$), 4.61 (br. d, J = 6.0 Hz, 2 H, OC$\underline{H}_2$-CH), 5.73 (br. dt, J_d = 15.3 Hz, J_t = 6.0 Hz, 1 H, CH$_2$-C$\underline{H}$=CH-CH$_3$), 5.84 (br. dq, J_d = 15.3 Hz, J_q = 6.2 Hz, 1 H, CH$_2$-CH=C$\underline{H}$-CH$_3$), 6.7 - 7.4 (m, 5 H, aromatic H). - ^{13}C-NMR: 11.03 (CH$_3$), 17.78 (CH$_3$), 23.23 (CH$_2$), 66.24 (CH$_2$), 121.03 (CH), 122.54 (CH), 126.07 (CH), 128.82 (CH), 129.97 (CH), 148.83 (C), 164.11 (C). - MS (GC/MS): 203 (17) [M$^+$], 188 (6) [M - CH$_3$], 174 (8) [M - C$_2$H$_5$], 132 (36) [M - CH$_3$-CH=CH-CH$_2$O], 93 (100) [Ph-NH$_2^+$], 55 (44) [CH$_3$-CH=CH-CH$_2^+$]. - Analysis: $C_{13}H_{17}NO$ (203.3) Calcd. C 76.80 H 8.43 Found C 76.71 H 8.45 .

(E)-2-Hexenyl N-Phenylpropanimidate (1e): Yield 72 %. - IR (film): 1665 (C=N), 1595 (C=C). - ^{1}H-NMR: 0.93 (t, J = 7.3 Hz, 3 H, CH$_2$-CH$_2$-C$\underline{H}_3$), 1.08 (t, J = 7.6 Hz, 3 H, N=C-CH$_2$-C$\underline{H}_3$), 1.44 (m$_c$, 2 H, CH$_2$-C$\underline{H}_2$-CH$_3$), 2.07 (dt, J_d = 7.1 Hz, J_t = 7.0 Hz, 2 H, CH-C$\underline{H}_2$-CH$_2$), 2.17 (q, J = 7.6 Hz, 2 H, N=C-C$\underline{H}_2$-CH$_3$), 4.62 (br. d, J = 5.8 Hz, 2 H, OC$\underline{H}_2$-CH), 5.70 (br. dt, J_d = 15.4 Hz, J_t = 5.8 Hz, 1 H, OCH$_2$-C$\underline{H}$=CH-CH$_2$), 5.81 (dt, J_d = 15.4 Hz, J_t = 6.5 Hz, 1 H, OCH$_2$-CH=C$\underline{H}$-CH$_2$), 6.7 - 7.4 (m, 5 H, aromatic H). - ^{13}C-NMR: 11.09 (CH$_3$), 13.64 (CH$_3$), 22.17 (CH$_2$), 23.31 (CH$_2$), 34.42 (CH$_2$), 66.31 (CH$_2$), 121.10 (CH), 122.57 (CH), 124.93 (CH), 128.87 (CH), 135.06 (CH), 148.92 (C), 164.17 (C). - MS: 231 (17) [M$^+$], 202 (26) [M - C$_2$H$_5$], 189 (20) [M - CH$_3$-CH=CH$_2$], 188 (19) [M - C$_3$H$_7$], 132 (48) [M - C$_3$H$_7$-CH=CH-CH$_2$O], 93 (100) [Ph-NH$_2^+$]. - Analysis: $C_{15}H_{21}NO$ (231.3) Calcd. 77.89 H 9.15 Found C 78.01 H 9.19 .

(Z)-2-Hexenyl N-Phenylpropanimidate (1f): Yield 66 %. - IR (film): 1665 (C=N), 1595 (C=C). - ^{1}H-NMR: 0.91 (t, J = 7.3 Hz, 3 H, CH$_2$-CH$_2$-C$\underline{H}_3$), 1.06 (t, J = 7.6 Hz, 3 H, N=C-CH$_2$-C$\underline{H}_3$), 1.41 (m, 2 H, CH$_2$-C$\underline{H}_2$-CH$_3$), 2.05 -2.20 (m, 4 H, CH-C$\underline{H}_2$-CH$_2$, N=C-C$\underline{H}_2$-CH$_3$), 4.72 (d, J = 5.3 Hz, 2 H, OC$\underline{H}_2$-CH), 5.58 - 5.73 (m, 2 H, C$\underline{H}$=C$\underline{H}$), 6.7 - 7.4 (m, 5 H, aromatic H). - ^{13}C-NMR: 11.07 (CH$_3$), 13.64 (CH$_3$), 22.63 (CH$_2$), 23.28 (CH$_2$), 29.66 (CH$_2$), 61.65 (CH$_2$), 121.10 (CH), 122.59 (CH), 124.62 (CH), 128.86 (CH), 134.10 (CH), 148.89 (C), 164.32 (C). - MS: 231 (4) [M$^+$], 202 (12) [M - C$_2$H$_5$], 189 (6) [M - CH$_3$-CH=CH$_2$], 188 (5) [M - C$_3$H$_7$], 132 (43) [M - C$_3$H$_7$-CH=CH-CH$_2$O], 93 (100) [Ph-NH$_2^+$]. - Analysis: $C_{15}H_{21}NO$ (231.3) Calcd. C 77.89 H 9.15 Found C 77.61 H 9.38 .

(E)-2-Methyl-2-butenyl N-Phenylpropanimidate (1g): Yield 61 %. - IR: 1655 (C=N), 1595 (C=C). - ^{1}H-NMR: 1.09 (t, J = 7.6 Hz, 3 H, CH_2-C$\underline{H}_3$), 1.67 (br. d, J = 6.7 Hz, 3 H, C=CH-C$\underline{H}_3$), 1.74 (s, 3 H, OCH_2-C-C$\underline{H}_3$), 2.19 (q, J = 7.6 Hz, 2 H, C$\underline{H}_2$-CH_3), 4.55 (s, 2 H, OCH_2), 5.61 (br. q, J = 6.7 Hz, 1 H, C=C$\underline{H}$-CH_3), 6.7 - 7.4 (m, 5 H, aromatic H). - ^{13}C-NMR: 11.06 (CH_3), 13.20 (CH_3), 13.73 (CH_3), 23.35 (CH_2), 71.31 (CH_2), 121.12 (CH), 122.57 (CH), 122.82 (CH), 128.86 (CH), 131.76 (C), 148.94 (C), 164.42 (C). - MS: 217 (3) [M$^+$], 202 (5) [M - CH_3], 132 (17) [M - CH_3-CH=C(CH_3)-CH_2O], 93 (100) [Ph-NH_2^+], 69 (51) [CH_3-CH=C(CH_3)-CH_2^+]. - Analysis: $C_{14}H_{19}NO$ (217.3) Calcd. C 77.38 H 8.81 Found C 77.13 H 8.67 .

3-Methyl-2-butenyl N-Phenylpropanimidate (1h): Yield 73 %. - IR: 1660 (C=N), 1600 (C=C). - ^{1}H-NMR: 1.07 (t, J = 7.5 Hz, 3 H, CH_2-C$\underline{H}_3$), 1.74 [s, 3 H, CH=C(CH_3)-C$\underline{H}_3$], 1.80 [s, 3 H, CH=C(CH_3)-C$\underline{H}_3$], 2.17 (q, J = 7.5 Hz, 2 H, C$\underline{H}_2$-CH_3), 4.67 (d, J = 6.9 Hz, 2 H, OC$\underline{H}_2$-CH), 5.48 (br. t, J = 7.0 Hz, 1 H, CH_2-C$\underline{H}$=C), 6.7 - 7.4 ((m, 5 H, aromatic H). - ^{13}C-NMR: 11.09 (CH_3), 18.07 (CH_3), 23.30 (CH_2), 25.75 (CH_3), 62.59 (CH_2), 119.69 (CH), 121.18 (CH), 122.60 (CH), 128.91 (CH), 137.74 (C), 149.06 (C), 164.54 (C). - MS: 217 (5) [M$^+$], 188 (3) [M - C_2H_5], 149 (37) [C_2H_5-CO-NHPh$^+$], 93 (100) [Ph-NH_2^+], 69 (53) [(CH_3)$_2$C=CH-CH_2^+]. - Analysis: $C_{14}H_{19}NO$ (217.3) Calcd. C 77.38 H 8.81 Found C 77.28 H 8.89 .

1-Methyl-2-propenyl N-Phenylpropanimidate (1i): Yield 37 %. - IR (film): 1665 (C=N), 1595 (C=C). - ^{1}H-NMR: 1.00 (t, J = 7.6 Hz, 3 H, CH_2-C$\underline{H}_3$), 1.31 (d, J = 6.5 Hz, 3 H, OCH-C$\underline{H}_3$), 2.08 (q, J = 7.6 Hz, 2 H, C$\underline{H}_2$-CH_3), 5.07 (br. d, J = 10.6 Hz, 1 H, CH=CH-$\underline{H}$), 5.22 (br. d, J = 17.3 Hz, 1 H, CH=CH-$\underline{H}$), 5.51 [m$_c$, 1 H, OC$\underline{H}$(CH_3)-CH], 5.89 (ddd, J = 5.3 Hz, J = 10.6 Hz, J = 17.3 Hz, 1 H, CH-C$\underline{H}$=CH_2), 6.6 -7.3 (m, 5 H, aromatic H). - ^{13}C-NMR: 11.08 (CH_3), 19.66 (CH_3), 23.43 (CH_2), 70.44 (CH), 114.53 (CH_2), 121.01 (CH), 122.49 (CH), 128.85 (CH), 138.79 (CH), 148.97 (C), 163.21 (C). - MS (GC / MS): 203 (26) [M$^+$], 188 (2) [M - CH_3], 174 (6) [M - C_2H_5], 132 (35) [M - CH_2=CH-CH(CH_3)O], 93 (100) [Ph-NH_2^+], 55 (33) [CH_2=CH-CH-CH_3^+]. - Analysis: $C_{13}H_{17}NO$ (203.3) Calcd. C 76.80 H 8.43 Found C 76.70 H 8.40 .

(E)-2-Butenyl N-Phenyl-2-methylpropanimidate (1j): Yield 50 %. - IR: 1665 (C=N), 1600 (C=C). - ^{1}-NMR: 1.08 [d, J = 6.7 Hz, 6 H, CH(C$\underline{H}_3$)$_2$], 1.75 (br. d, J = 6.1 Hz, 3 H, CH=CH-C$\underline{H}_3$), 2.65 [sept, J = 6.7 Hz, 1 H, C$\underline{H}$(CH_3)$_2$], 4.59 (br. d, J = 5.7 Hz, 2 H, OC$\underline{H}_2$-CH), 5.70 (br. dt, J_d = 15.3 Hz, J_t = 5.7 Hz, 1 H, OCH_2-C$\underline{H}$=CH), 5.81 (br. dq, J_d = 15.3 Hz, J_q = 6.1 Hz, 1 H, CH=C$\underline{H}$-CH_3), 6.7 - 7.4 (m, 5 H, aromatic H). - ^{13}C-NMR: 17.86 (CH_3), 19.85 (CH_3), 28.88 (CH), 66.02 (CH_2), 121.02 (CH), 122.43 (CH), 126.23 (CH), 128.89 (CH), 129.38 (CH), 148.89 (C), 166.45 (C). - MS (GC / MS): 217 (31) [M$^+$], 202 (8) [M - CH_3], 174 (13) [M - CH(CH_3)$_2$], 146 (45) [M - CH_3-CH=CH-CH_2O], 93 (100) [Ph-NH_2^+], 55 (80) [CH_3-CH=CH-CH_2^+], 43 (81) [CH(CH_3)$_2^+$]. - Analysis: $C_{14}H_{19}NO$ (217.3) Calcd. C 77.38 H 8.81 Found C 77.26 H 8.85 .

3-Methyl-2-butenyl N-Phenyl-2-methylpropanimidate (1k): Yield 66 %. - IR: 1655 (C=N), 1595 (C=C). - ^{1}H-NMR: 1.07 [d, J = 6.7 Hz, 6 H, CH(C$\underline{H}_3$)$_2$], 1.73 [s, 3 H, CH=C(CH_3)-C$\underline{H}_3$], 1.80 [s, 3 H, CH=C(CH_3)-C$\underline{H}_3$], 2.65 [sept, J = 6.7 Hz, 1 H, C$\underline{H}$(CH_3)$_2$], 4.65 (d, J = 6.8 Hz, 2 H, OC$\underline{H}_2$-CH), 5.46 (br. t, J = 6.8 Hz, 1 H, OCH_2-C$\underline{H}$), 6.7 - 7.4 (m, 5 H, aromatic H). - ^{13}C-NMR: 18.12 (CH_3), 19.80 (CH_3), 25.71 (CH_3), 28.89 (CH), 62.46 (CH_2), 119.88 (CH), 121.09 (CH), 122.42 (CH), 128.91 (CH), 137.21 (C), 149.06 (C), 166.75 (C). - MS (GC / MS): 231 (26) [M$^+$], 188 (4) [M - CH(CH_3)$_2$], 163 (48) [(CH_3)$_2$CH-CO-NHPh$^+$], 93 (100) [Ph-NH_2^+], 69 (52) [(CH_3)$_2$C=CH-CH_2^+]. - Analysis: $C_{15}H_{21}NO$ (231.3) Calcd. C 77.89 H 9.15 Found C 77.73 H 9.16 .

(E)-2-Butenyl N-Phenyl-2-phenylacetimidate (1l): Yield 62 %. - IR: 1660 (C=N), 1590 (C=C). - ^{1}H-NMR: 1.74 (br. d, J = 6.0 Hz, 3 H, CH-C$\underline{H}_3$), 3.52 (s, 2 H, C$\underline{H}_2$-Ph), 4.64 (br. d, J = 5.8 Hz, 2 H, OC$\underline{H}_2$-CH), 5.70 (br. dt, J_d = 15.4 Hz, J_t = 5.8 Hz, 1 H, OCH_2-C$\underline{H}$=CH), 5.80 (br. dq, J_d = 15.4 Hz, J_q = 6.0 Hz, 1 H, CH=C$\underline{H}$-CH_3), 6.7 - 7.4 (m, 10 H, aromatic H). - ^{13}C-NMR: 17.82 (CH_3), 36.16 (CH_2), 66.63 (CH_2), 121.35 (CH), 122.91 (CH), 125.96 (CH), 126.48 (CH), 128.34 (CH), 128.88 (CH), 128.92 (CH), 130.07 (CH), 135.88 (C), 148.53 (C), 160.86 (C). - MS (GC / MS): 265 (11) [M$^+$], 211 (5) [Ph-CH_2-CO-NHPh$^+$], 194 (7) [M - CH_3-CH=CH-CH_2O], 174 (16) [M - Ph-CH_2], 93 (85) [Ph-NH_2^+], 91 (100) [$C_7H_7^+$], 55 (82), [CH_3-CH=CH-CH_2^+]. - Analysis: $C_{18}H_{19}NO$ (265.4) Calcd. C 81.46 H 7.22 Found C 81.58 H 7.25 .

Amides 3. - General procedure: A 0.2 M solution of the allylimidate 1 in decalin was stirred under reflux until GC (or TLC for 1l) indicated total consumption of 1 (see Table 1 for reaction times). After distillative removal of the solvent in vacuo the rearranged amide 3 was isolated by flash chromatography. Reactions were run on a 1 - 3.5 mmol scale.

N-Phenyl-3-methyl-4-pentenamide (3a): Yield 38 % after flash chromatography (ethyl acetate / petrolether 1 : 4). - m.p. 66 - 67 °C. - IR: 1690 (C=O), 1605 (C=C). - ^{1}H-NMR: 1.13 (d, 6.8 Hz, 3 H, C$\underline{H}_3$-CH), 2.31 (dd, J = 14.4 Hz, J = 7.1 Hz, 1 H, CH-CH-$\underline{H}$), 2.41 (dd, J = 14.4 Hz, J = 7.4 Hz, 1 H, CH-CH-$\underline{H}$), 2.80 (m_c, 1 H, C$\underline{H}$-CH$_3$), 5.03 (br. d, J = 10.4 Hz, 1 H, CH=CH-$\underline{H}$), 5.11 (br. d, J = 17.2 Hz, 1 H, CH=CH-$\underline{H}$), 5.85 (ddd, J = 17.3 Hz, J = 10.3 Hz, J = 7.0 Hz, 1 H, CH-C$\underline{H}$=CH$_2$), 7.0 - 7.6 (m, 5 H, aromatic H). - ^{13}C-NMR: 19.71 (CH$_3$), 34.84 (CH), 44.71 (CH$_2$), 113.89 (CH$_2$), 119.91 (CH), 124.27 (CH), 128.96 (CH), 137.8 (C), 142.65 (CH), 170.1 (C). - MS: 189 (3) [M$^+$], 93 (100) [Ph-NH$_2^+$], 69 (20) [M - CO-NHPh], 55 (45) [CH$_2$=CH-CH-CH$_3^+$], 41 (78) [CH$_2$=CH-CH$_2^+$]. - Analysis: $C_{12}H_{15}NO$ (189.3) Calcd. C 76.14 H 7.99 Found C 76.10 H 8.08 .

N-Phenyl-3,3-dimethyl-4-pentenamide (3b): GC indicated the presence of 10 % 3b in the product mixture. - MS (GC / MS): 203 (12) [M$^+$], 135 (5) [CH$_3$-CO-NHPh$^+$], 93 (100) [Ph-NH$_2^+$], 69 (26) [CH$_2$=CH-C(CH$_3$)$_2^+$].

N-Phenyl-2-methyl-4-pentenamide (3c): Yield 55 % after flash chromatography (ethyl acetate / petrolether 1 : 4). - m.p. 90 - 91°C. - IR: 1685 (C=O), 1600 (C=C). - ^{1}H-NMR: 1.25 (d, 6.7 Hz, 3 H, C$\underline{H}_3$-CH), 2.17 - 2.30 (m, 1 H, C$\underline{H}$-CH$_3$), 2.37 - 2.55 (m, 2 H, CH-C$\underline{H}_2$), 5.06 (br. d, J = 10.3 Hz, 1 H, CH=CH-$\underline{H}$), 5.12 (br. d, J = 17.2 Hz, 1 H, CH=CH-$\underline{H}$), 5.73 - 5.92 (m, 1 H, CH$_2$=C$\underline{H}$-CH$_2$), 7.0 - 7.6 (m, 5 H, aromatic H). - ^{13}C-NMR: 17.41 (CH$_3$), 38.37 (CH$_2$), 42.19 (CH), 117.19 (CH$_2$), 119.89 (CH), 124.18 (CH), 128.93 (CH), 135.61 (CH), 137.91 (C), 174.07 (C). - MS (GC / MS): 189 (36) [M$^+$], 174 (4) [M - CH$_3$], 147 (3) [M - CH$_3$-CH=CH$_2$], 93 (100) [Ph-NH$_2^+$], 69 (61) [M - CO-NHPh], 41 (88) [CH$_2$=CH-CH$_2^+$]. - Analysis $C_{12}H_{15}NO$ (189.3) Calcd. C 76.14 H 7.99 Found C 76.00 H 8.11 .

syn-N-Phenyl-2,3-dimethyl-4-pentenamide (syn-3d) and **anti-N-Phenyl-2,3-dimethyl-4-pentenamide (anti-3d)**: Yield 69 % (syn : anti = 2 : 1 by capillary GC) after flash chromatography (ethyl acetate / petrolether 1 : 6). HPLC separation (ethyl acetate / petrolether 1 : 4) afforded samples of the pure stereoisomers. -
Data of **syn-3d**: m.p. 48 - 50°C. - IR (KBr): 1650 (C=O), 1600 (C=C). - ^{1}H-NMR: 1.08 (d, J = 6.9 Hz, 3 H, CH$_2$=CH-CH-C$\underline{H}_3$), 1.22 (d, J = 7.0 Hz, 3 H, CO-CH-C$\underline{H}_3$), 2.27 (m_c, simplified to d with J = 7.5 Hz on irradiation at 1.22 ppm, 1 H, CO-C$\underline{H}$-CH$_3$), 2.51 (m_c, simplified to dd with J = 7.6 Hz and J = 7.6 Hz on irradiation at 1.08 ppm, 1 H, CH$_2$=CH-C$\underline{H}$-CH$_3$), 5.01 (br. d, J = 10.2 Hz, 1 H, CH=CH-$\underline{H}$), 5.07 (br. d, J = 17.2 Hz, 1 H, CH=CH-$\underline{H}$), 5.83 (ddd, J = 17.4 Hz, J = 10.2 Hz, J = 7.5 Hz, 1 H, CH$_2$=C$\underline{H}$-CH), 7.0 - 7.6 (m, 5 H, aromatic H). - ^{13}C-NMR: 14.70 (CH$_3$), 16.51 (CH$_3$), 40.79 (CH), 47.17 (CH), 114.32 (CH$_2$), 120.35 (CH), 124.03 (CH), 128.66 (CH), 137.95 (C), 141.46 (CH), 174.41 (C). - MS: 203 (7) [M$^+$], 188 (7) [M - CH$_3$], 149 (6) [C$_2$H$_5$-CO-NHPh$^+$], 147 (9) [M - CH$_3$-CH=CH-CH$_3$], 93 (91) [Ph-NH$_2^+$], 83 (32) [M - CO-NHPh], 55 (100) [CH$_2$=CH-CH-CH$_3^+$]. - Analysis: $C_{13}H_{17}NO$ (203.3) Calcd. C 76.80 H 8.43 Found C 76.63 H 8.65 .
Data of **anti-3d**: m.p. 94 - 95°C. - IR: 1685 (C=O), 1600 (C=C). - ^{1}H-NMR: 1.08 (d, J = 6.7 Hz, 3 H, CH$_2$=CH-CH-C$\underline{H}_3$), 1.21 (d, J = 6.9 Hz, 3 H, CO-CH-C$\underline{H}_3$), 2.18 (m_c, simplified to d with J = 8.0 Hz on irradiation at 1.21 ppm, 1 H, CO-C$\underline{H}$-CH$_3$), 2.49 (m_c, simplified to dd with J = 8.2 Hz and J = 8.3 Hz on irradiation at 1.08 ppm, 1 H, CH$_2$=CH-C$\underline{H}$-CH$_3$), 5.08 (br. d, J = 10.2 Hz, 1 H, CH=CH-$\underline{H}$), 5.10 (br. d, J = 17.2 Hz, 1 H, CH=CH-$\underline{H}$), 5.71 (ddd, J = 17.2 Hz, J = 10.2 Hz, J = 8.3 Hz, 1 H, CH$_2$=C$\underline{H}$-CH), 7.0 - 7.6 (m, 5 H, aromatic H). - ^{13}C-NMR: 15.87 (CH$_3$), 18.36 (CH$_3$), 41.60 (CH), 47.55 (CH), 115.23 (CH$_2$), 120.02 (CH), 124.11 (CH), 128.82 (CH), 137.78 (C), 141.29 (CH), 174.28 (C). - MS: 203 (6) [M$^+$], 188 (7) [M - CH$_3$], 149 (10) [C$_2$H$_5$-CO-NHPh$^+$], 147 (6) [M - CH$_3$-CH=CH-CH$_3$], 93 (84) [Ph-NH$_2^+$], 83 (39) [M - CO-NHPh], 55 (100) [CH$_2$=CH-CH-CH$_3^+$]. - Analysis: $C_{13}H_{17}NO$ (203.3) Calcd. C 76.80 H 8.43 Found C 76.82 H 8.49 .

syn-N-Phenyl-2-methyl-3-propyl-4-pentenamide (syn-3e) and **anti-N-Phenyl-2-methyl-3-propyl-4-pentenamide (anti-3e)**: From 1e: Yield 65 % (syn : anti = 2.0 : 1 by capillary GC) after flash chromatography (ethyl acetate / petrolether 1 : 6). From 1f: Yield 26 % (syn : anti = 1 : 1.6 by capillary GC) after flash chromatography (ethyl acetate / petrolether 1 : 6), followed by HPLC (ethyl acetate / petrolether 1 : 4). HPLC separation (ethyl acetate / petrolether 1 : 4) afforded samples of the pure stereoisomers. -
Data of **syn-3e**: Amorphous solid. - IR: 1685 (C=O), 1600 (C=C). - ^{1}H-NMR: 0.89 (t, J = 7.0 Hz, 3 H, CH_2-C$\underline{H}_3$), 1.1 - 1.6 (m, 7 H, including d with J = 6.6 Hz at 1.24 ppm, CO-CH-C$\underline{H}_3$, C$\underline{H}_2$-C$\underline{H}_2$-CH_3), 2.2 - 2.4 (m, 2 H, CO-C$\underline{H}$-CH_3, CH-C$\underline{H}$-CH_2), 5.0 - 5.1 (m, 2 H, C$\underline{H}_2$=CH-CH), 5.68 (m_c, 1 H, CH_2=C$\underline{H}$-CH), 7.0 - 7.6 (m, 5 H, aromatic H). - ^{13}C-NMR: 13.99, 15.26, 20.30, 33.55, 47.01, 47.36, 116.59, 119.94, 124.18, 128.95, 137.81, 139.61, 173.52 . - MS (GC / MS): 231 (11) [M$^+$], 216 (2) [M - CH_3], 188 (49) [M - CH_2-CH_2-CH_3], 149 (15) [C_2H_5-CO-NHPh$^+$], 93 (100) [Ph-NH_2^+], 69 (61) [M - CO-NHPh - CH_3-CH=CH_2], 55 (53) [$C_4H_7^+$], 41 (44) [$C_3H_5^+$]. - Analysis: $C_{15}H_{21}NO$ (231.3) Calcd. C 77.89 H 9.15 Found C 77.79 H 9.00 .
Data of **anti-3e**: m.p. 109 - 110°C. - IR: 1685 (C=O), 1600 (C=C). - ^{1}H-NMR: 0.86 (t, J = 7.0 Hz, 3 H, CH_2-C$\underline{H}_3$), 1.1 - 1.6 (m, 7 H, including d with J = 6.8 Hz at 1.19 ppm, CO-CH-C$\underline{H}_3$, C$\underline{H}_2$-C$\underline{H}_2$-CH_3), 2.22 (m_c, simplified to d with J = 8.2 Hz on irradiation at 1.19 ppm, 1 H, CO-C$\underline{H}$-CH_3), 2.34 (m_c, 1 H, CH-C$\underline{H}$-CH_2), 5.10 (dd, J = 1.8 Hz, J = 17.2 Hz, 1 H, $\underline{H}$-CH=CH), 5.14 (dd, J = 1.8 Hz, J = 10.5 Hz, 1 H, $\underline{H}$-CH=CH), 5.52 (m_c, 1 H, CH_2=C$\underline{H}$-CH), 7.0 - 7.6 (m, 5 H, aromatic H). - ^{13}C-NMR: 13.93 (CH_3), 15.77 (CH_3), 20.47 (CH_2), 34.79 (CH_2), 47.08 (CH), 47.48 (CH), 117.23 (CH_2), 119.84 (CH), 124.23 (CH), 129.00 (CH), 137.88 (C), 139.63 (CH), 174.10 (C). - MS (GC / MS): 231 (12) [M$^+$], 216 (4) [M - CH_3], 188 (21) [M - CH_2-CH_2-CH_3], 149 (22) [C_2H_5-CO-NHPh$^+$], 93 (100) [Ph-NH_2^+], 69 (57) [M - CO-NHPh - CH_3-CH=CH_2], 55 (47) [$C_4H_7^+$], 41 (39) [$C_3H_5^+$]. - Analysis: $C_{15}H_{21}NO$ (231.3) Calcd. C 77.89 H 9.15 Found C 77.70 H 9.34 .

syn-N-Phenyl-2,3,4-trimethyl-4-pentenamide (syn-3g) and **anti-N-Phenyl-2,3,4-trimethyl-4-pentenamide (anti-3g)**: Yield 62 % (syn : anti = 3.5 : 1 by capillary GC) after flash chromatography (ethyl acetate / petrolether 1 : 6). HPLC separation (ethyl acetate / petrolether 1 : 7) afforded samples of the pure stereoisomers. -
Data of **syn-3g**: m.p. 72 - 73°C. - IR: 1680 (C=O), 1595 (C=C). - ^{1}H-NMR: 1.09 (d, J = 6.8 Hz, 3 H, CH_2=C-CH-C$\underline{H}_3$), 1.22 (d, J = 6.7 Hz, 3 H, CO-CH-C$\underline{H}_3$), 1.76 (s, 3 H, CH_2=C-C$\underline{H}_3$), 2.41 (dq, J_d = 8.6 Hz, J_q = 6.7 Hz, 1 H, CH_3-C$\underline{H}$-CH), 2.52 (dq, J_d = 8.7 Hz, J_q = 6.7 Hz, 1 H, CH_3-C$\underline{H}$-CH), 4.80 (s, 2 H, C$\underline{H}_2$=C), 7.0 - 7.6 (m, 5 H, aromatic H). - ^{13}C-NMR: 14.63 (CH_3), 16.27 (CH_3), 20.63 (CH_3), 43.76 (CH), 46.15 (CH), 111.07 (CH_2), 119.99 (CH), 124.10 (CH), 128.88 (CH), 137.97 (C), 148.49 (C), 174.11 (C). - MS (GC / MS): 217 (10) [M$^+$], 202 (12) [M - CH_3], 149 (6) [C_2H_5-CO-NHPh$^+$], 93 (100) [Ph-NH_2^+], 83 (44) [$C_6H_{11}^+$], 55 (65) [$C_4H_7^+$], 41 (74) [$C_3H_5^+$]. - Analysis: $C_{14}H_{19}NO$ (217.3) Calcd. C 77.38 H 8.81 Found C 77.4 H 8.9 .
Data of **anti-3g**: m.p. 96 - 97°C. - IR: 1675 (C=O), 1600 (C=C). - ^{1}H-NMR: 1.08 (d, J = 6.8 Hz, 3 H, CH_2=C-CH-C$\underline{H}_3$), 1.15 (d, J = 6.8 Hz, 3 H, CO-CH-C$\underline{H}_3$), 1.67 (s, 3 H, CH_2=C-C$\underline{H}_3$), 2.24 (dq, J_d = 9.8 Hz, J_q = 6.8 Hz, 1 H, CH_3-C$\underline{H}$-CH), 2.48 (dq, J_d = 9.8 Hz, J_q = 6.8 Hz, 1 H, CH_3-C$\underline{H}$-CH), 4.83 (s, 2 H, C$\underline{H}_2$=C), 7.0 - 7.6 (m, 5 H, aromatic H). - ^{13}C-NMR: 16.81, 17.94, 18.55, 45.13, 46.41, 112.40, 119.86, 124.25, 128.99, 137.87, 146.99, 174.22. - MS (GC / MS): 217 (13) [M$^+$], 202 (12) [M - CH_3], 149 (7) [C_2H_5-CO-NHPh$^+$], 93 (100) [Ph-NH_2^+], 83 (39) [$C_6H_{11}^+$], 55 (54) [$C_4H_7^+$], 41 (48) [$C_3H_5^+$]. - Analysis: $C_{14}H_{19}NO$ (217.3) Calcd. C 77.38 H 8.81 Found C 77.46 H 8.96 .

N-Phenyl-2,3,3-trimethyl-4-pentenamide (3h): Yield 20 % after flash chromatography (ethyl acetate / petrolether 1 : 9) followed by HPLC (ethyl acetate / petrolether 1 : 9). - m.p. 78 - 79°C. - IR: 1675 (C=O), 1595 (C=C). - ^{1}H-NMR: 1.13 (s, 3 H, CH_3-C), 1.16 (s, 3 H, CH_3-C), 1.20 (d, J = 7.0 Hz, 3 H, C$\underline{H}_3$-CH), 2.23 (q, J = 7.0 Hz, 1 H, CH_3-C$\underline{H}$), 5.07 (dd, J = 1.2 Hz, J = 17.4 Hz, 1 H, CH=CH-$\underline{H}$), 5.11 (dd, J = 1.2 Hz, J = 10.8 Hz, 1 H, CH=CH-$\underline{H}$), 5.98 (dd, J = 10.8 Hz, J = 17.4 Hz, 1 H, C$\underline{H}$=CH_2), 7.0 - 7.6 (m, 5 H, aromatic H). - ^{13}C-NMR: 13.15 (CH_3), 24.13 (CH_3), 25.10 (CH_3), 39.03 (C), 51.96 (CH), 112.71 (CH_2), 119.91 (CH), 124.17 (CH), 128.95 (CH), 137.84 (C), 145.95 (CH), 173.22 (C). - MS (GC / MS): 217 (7) [M$^+$], 202 (5) [M - CH_3], 149 (19) [C_2H_5-CO-NHPh$^+$], 93 (100) [Ph-NH_2^+], 69 (49) [CH_2=CH-C(CH_3)$_2^+$], 55 (54) [$C_4H_7^+$], 41 (64) [$C_3H_5^+$]. - Analysis: $C_{14}H_{19}NO$ (217.3) Calcd. C 77.38 H 8.81 Found C 77.4 H 8.8 .

(E)-N-Phenyl-2-methyl-4-hexenamide (3l): Yield 65 % (E : Z = 97.2 : 2.8 by capillary GC) after flash chromatography (ethyl acetate / CH_2Cl_2 1 : 50). - m.p. 100 - 101°C. - IR: 1680 (C=O), 1600 (C=C). - ^{1}H-NMR: 1.23 (d, J = 6.6 Hz, 3 H, CO-CH-C$\underline{H}_3$), 1.66 (br. d, J = 6.0 Hz, 3 H, C$\underline{H}_3$-CH=CH), 2.10 - 2.25 (m, 1 H, CO-C$\underline{H}$-CH_3), 2.30 - 2.50 (m, 2 H, CH=CH-C$\underline{H}_2$), 5.37 - 5.62 (m, 2 H, including dq with J_d = 15.2 Hz and J_q = 6.1 Hz at 5.56 ppm, C$\underline{H}$=C$\underline{H}$), 7.0 - 7.6 (m, 5 H, aromatic H). - ^{13}C-NMR: 17.37, 17.93, 37.31, 42.73, 119.82, 124.17, 128.00, 128.06, 128.98, 137.94, 174.21 . - MS (GC / MS): 203 (50) [M$^+$], 188 (9) [M - CH_3], 149 (8) [C_2H_5-CO-NHPh$^+$], 93 (100) [Ph-NH_2^+], 83 (22) [M - CO-NHPh], 55 (47) [CH_3-CH=CH-CH_2^+]. - Analysis: $C_{13}H_{17}NO$ (203.3) Calcd. C 76.80 H 8.43 Found C 76.78 H 8.69 .

N-Phenyl-2,2,3-trimethyl-4-pentenamide (3j): Yield 73 % after flash chromatography (ethyl acetate / CH_2Cl_2 1 : 19). - m.p. 51 - 52°C. - IR: 1675 (C=O), 1600 (C=C). - ^{1}H-NMR: 0.97 (d, J = 6.9 Hz, 3 H, CH-C$\underline{H}_3$), 1.17 [s, 6 H, C(C$\underline{H}_3$)$_2$], 2.50 (dq, J_d = 8.0 Hz, J_q = 6.9 Hz, 1 H, CH-C$\underline{H}$-CH_3), 5.00 - 5.08 (m, 2 H, C$\underline{H}_2$=CH), 5.75 (ddd, J = 8.0 Hz, J = 9.7 Hz, J = 17.8 Hz, 1 H, CH_2=C$\underline{H}$-CH), 7.0 - 7.5 (m, 5 H, aromatic H). - ^{13}C-NMR: 14.91 (CH_3), 21.46 (CH_3), 23.45 (CH_3), 45.45 (CH), 45.88 (C), 116.20 (CH_2), 120.09 (CH), 124.26 (CH), 128.94 (CH), 137.83 (C), 139.61 (CH), 175.59 (C). - MS: 217 (15) [M$^+$], 202 (10) [M - CH_3], 163 (18) [M - CH_2=CH-CH=CH_2], 161 (12) [M - CH_3-CH=CH-CH_3], 97 (50) [M - CO-NHPh], 93 (57) [Ph-NH_2^+], 69 (51) [M - CH_3-CH=CH-CH_3 - NHPh], 55 (100) [CH_2=CH-CH-CH_3^+], 41 (60) [$C_3H_5^+$]. - Analysis: $C_{14}H_{19}NO$ (217.3) Calcd. C 77.38 H 8.81 Found C 77.22 H 9.03 .

N-Phenyl-2,2,3,3,-tetramethyl-4-pentenamide (3k): GC indicated the presence of 6 % 3k in the product mixture. - MS (GC / MS): 231 (13) [M$^+$], 216 (4) [M - CH_3], 163 (65) [$(CH_3)_2$CH-CO-NHPh$^+$], 162 (24) [M - CH_2=CH-C$(CH_3)_2$], 161 (46) [CH_2=C(CH_3)-CO-NHPh$^+$], 111 (51) [CH_2=CH-C$(CH_3)_2$-C$(CH_3)_2^+$], 93 (65) [Ph-NH_2^+], 69 (100) [CH_2=CH-C$(CH_3)_2^+$].

syn-N-Phenyl-3-methyl-2-phenyl-4-pentenamide (syn-3l) and **anti-N-Phenyl-3-methyl-2-phenyl-4-pentenamide (anti-3l)**: Yield 93 % (syn : anti = 1.6 : 1 by ^{1}H-NMR) after flash chromatography (ethyl acetate / CH_2Cl_2 1 : 9). The stereoisomers could not be separated by HPLC. - IR: 1685 (C=O), 1595 (C=C). - ^{1}H-NMR: 0.86 (d, J = 6.7 Hz, 3 H, C$\underline{H}_3$-CH, syn-3l), 1.20 (d, J = 6.5 Hz, 3 H, C$\underline{H}_3$-CH, anti-3l), 3.03 - 3.29 (m, 2 H, CH_3-C$\underline{H}$, Ph-C$\underline{H}$, syn-3l and anti-3l), 4.86 (br. d, J = 10.7 Hz, 1 H, CH=CH-$\underline{H}$, anti-3l), 4.91 (br. d, J = 17.7 Hz, 1 H, CH=CH-$\underline{H}$, anti-3l), 5.04 (br. d, J = 10.6 Hz, 1 H, CH=CH-$\underline{H}$, syn-3l), 5.18 (br. d, J = 17.1 Hz, 1 H, CH=CH-$\underline{H}$, syn-3l), 5.57 (ddd, J = 7.2 Hz, J = 10.4 Hz, J = 17.4 Hz, 1 H, CH-C$\underline{H}$=CH_2, anti-3l), 5.93 (ddd, J = 7.2 Hz, J = 10.4 Hz, J = 17.4 Hz, 1 H, CH-C$\underline{H}$=CH_2, syn-3l), 7.0 - 7.6 (m, 10 H, aromatic H, syn-3l and anti-3l). - ^{13}C-NMR: 17.45 (CH_3, syn-3l), 18.63 (CH_3, anti-3l), 40.46 (CH, syn-3l and anti-3l), 60.84 (CH, anti-3l), 60.89 (CH, syn-3l), 114.88 (CH_2, syn-3l and anti-3l), 119.88 (CH), 119.92 (CH), 124.24 (CH), 124.32 (CH), 127.38 (CH), 127.46 (CH), 128.43 (CH), 128.58 (CH), 128.62 (CH), 128.68 (CH), 128.85 (CH), 128.89 (CH), 137.76 (C), 138.03 (C), 138.10 (C), 140.74 (CH, anti-3l), 141.50 (CH, syn-3l), 170.85 (C, syn-3l), 170.97 (C, anti-3l). - MS: 265 (16) [M$^+$], 250 (5) [M - CH_3], 211 (20) [PhCH_2-CO-NHPh$^+$], 93 (100) [Ph-NH_2^+], 91 (82) [$C_7H_7^+$], 55 (70) [CH_2=CH-CH-CH_3^+]. - Analysis: $C_{18}H_{19}NO$ (265.4) Calcd. C 81.46 H 7.22 Found C 81.19 H 7.25 .

Allyl esters 6. - General procedure [10]: A 0.25 M solution of the required allylic alcohol in CH_2Cl_2 containing 1.1 equivalents of pyridine was cooled to 0°C. After the addition of a 1.5 M solution of the required acid chloride (1 equivalent) in CH_2Cl_2 the cooling bath was removed and the mixture was stirred at room temp. for 20 h. The reaction mixture was washed successively with 2 N HCl, satd. $NaHCO_3$ solution, and brine. The organic layer was dried over Na_2SO_4, and the solvent was removed by distillation at ambient pressure. Bulb-to-bulb distillation in vacuo yielded the allyl ester 6. Reactions were run on a 10 - 40 mmol scale.

(E)-2-Butenyl Propanoate (6a) [10]: Yield 60 %. - b.p. 70°C / 15 Torr. - IR (film): 1740 (C=O). - ^{1}H-NMR: 1.15 (t, J = 7.6 Hz, 3 H, CH_2-C$\underline{H}_3$), 1.73 (br. d, J = 6.4 Hz, 3 H, CH=CH-C$\underline{H}_3$), 2.34 (q, J = 7.6 Hz, 2 H, C$\underline{H}_2$-CH_3), 4.51 (br. d, J = 6.4 Hz, 2 H, OC$\underline{H}_2$-CH), 5.60 (qtd, J_q = 1.5 Hz, J_t = 6.4 Hz, J_d = 15.3 Hz, 1 H, CH_2-C$\underline{H}$=CH-CH_3), 5.80 (tqd, J_t = 0.9 Hz, J_q = 6.4 Hz, J_d = 15.3 Hz, 1 H, CH_2-CH=C$\underline{H}$-CH_3). - ^{13}C-NMR: 8.96 (CH_3), 17.61 (CH_3), 27.46 (CH_2), 64.94 (CH_2), 125.16 (CH), 131.07 (CH), 174.15 (C). - MS: 128 (3) [M$^+$], 99 (4) [M - C_2H_5], 71 (28) [M - C_2H_5-CO], 57 (100) [C_2H_5-CO$^+$], 55 (77) [CH_3-CH=CH-CH_2^+].

(E)-2-Hexenyl Propanoate (6b) [19]: Yield 69 %. - b.p. 90°C / 15 Torr. - IR (film): 1740 (C=O). - ^{1}H-NMR: 0.90 (t, J = 7.4 Hz, 3 H, CH_2-CH_2-C$\underline{H}_3$), 1.14 (t, J = 7.5 Hz, 3 H, CO-CH_2-C$\underline{H}_3$), 1.41 (m_c, 2 H, CH_2-C$\underline{H}_2$-CH_3), 2.04 (m_c, 2 H, CH-C$\underline{H}_2$-CH_2), 2.34 (q, J = 7.5 Hz, 2 H, CO-C$\underline{H}_2$-CH_3), 4.52 (br. d, J = 6.2 Hz, 2 H, OC$\underline{H}_2$-CH), 5.57 (ttd, J_t = 1.3 Hz, J_t = 6.5 Hz, J_d = 15.4 Hz, 1 H, OCH_2-C$\underline{H}$=CH-CH_2), 5.77 (ttd, J_t = 0.8 Hz, J_t = 6.6 Hz, J_d = 15.4 Hz, 1 H, OCH_2-CH=C$\underline{H}$-CH_3). - ^{13}C-NMR: 9.03 (CH_3), 13.54 (CH_3), 21.99 (CH_2), 27.53 (CH_2), 34.24 (CH_2), 65.06 (CH_2), 124.01 (CH), 136.15 (CH), 174.18 (C). - MS: 156 (1) [M$^+$], 127 (3) [M - C_2H_5], 100 (12) [M - CH_3-CH=C=O], 82 (30) [M - C_2H_5-CO_2H], 57 (100) [C_2H_5-CO$^+$].

(E)-2-Methyl-2-butenyl Propanoate (6c): Yield 61 %. - b.p. 80°C / 15 Torr. - IR (film): 1740 (C=O). - ^{1}H-NMR: 1.15 (t, J = 7.6 Hz, 3 H, CH_2-C$\underline{H}_3$), 1.63 (br. d, J = 6.8 Hz, 3 H, C=CH-C$\underline{H}_3$), 1.65 (s, 3 H, CH=C-C$\underline{H}_3$), 2.35 (q, J = 7.6 Hz, 2 H, C$\underline{H}_2$-CH_3), 4.47 (s, 2 H, OCH_2), 5.55 (br. q, J = 6.7 Hz, 1 H, C=C$\underline{H}$-CH_3). - ^{13}C-NMR: 9.09 (CH_3), 13.15 (CH_3), 13.53 (CH_3), 27.57 (CH_2), 70.07 (CH_2), 123.88 (CH), 130.86 (C), 174.31 (C). - MS (GC / MS): 142 (12) [M$^+$], 113 (2) [M - C_2H_5], 86 (29) [M - CH_3-CH=C=O], 68 (53) [M - C_2H_5-CO_2H], 57 (100) [C_2H_5-CO$^+$]. - Analysis: $C_8H_{14}O_2$ (142.2) Calcd. C 67.57 H 9.92 Found C 67.74 H 9.83 .

(E)-2-Butenyl 2-Phenylacetate (6d) [20]: Yield 72 %. - b.p. 90°C / 0.01 Torr. - IR (film): 1725 (C=O). - ^{1}H-NMR: 1.71 (br. d, J = 6.4 Hz, 3 H, CH-C$\underline{H}_3$), 3.62 (s, 2 H, C$\underline{H}_2$-Ph), 4.52 (br. d, J = 6.4 Hz, 2 H, OC$\underline{H}_2$-CH), 5.58 (qtd, J_q = 1.5 Hz, J_t = 6.4 Hz, J_d = 15.4 Hz, 1 H, OCH_2-C$\underline{H}$=CH-CH_3), 5.77 (tqd, J_t = 1.0 Hz, J_q = 6.4 Hz, J_d = 15.4 Hz, 1 H, OCH_2-CH=C$\underline{H}$-CH_3), 7.2 - 7.4 (m, 5 H, aromatic H). - ^{13}C-NMR: 17.69 (CH_3), 41.29 (CH_2), 65.52 (CH_2), 124.92 (CH), 126.97 (CH), 128.46 (CH), 129.19 (CH), 131.37 (CH), 133.97 (C), 171.29 (C). - MS (GC / MS): 190 (13) [M$^+$], 91 (100) [$C_7H_7^+$], 55 (63) [CH_3-CH=CH-CH_2^+].

Preparation of amides 3 via Ireland-Claisen rearrangement of allyl esters 6. - The general procedure given in ref. 10 (enolization in THF, quenching with TBDMS-Cl) was applied. The diastereomeric ratio of crude acid 7 was determined by ^{1}H-NMR. Conversion of acid 7 to amide 3 was performed as follows:
Crude acid 7 was stirred with 10 equivalents of $(COCl)_2$ at 40°C for 2 h. After distillative removal of excess oxalyl chloride in vacuo the residue was dissolved in dioxane (2 ml / mmol 7). This solution was added to a solution of 3 equivalents of aniline in dioxane (0.5 ml / mmol aniline) cooled to 0°C. After stirring for 2 h at room temp. the reaction mixture was diluted with CH_2Cl_2 and washed successively with 2 N HCl, satd. $NaHCO_3$ solution, and water. The organic layer was dried over Na_2SO_4, and the solvent was removed in vacuo. Flash chromatography gave the amide 3 as diastereomeric mixture.

3d: From ester 6a via acid 7a (anti : syn = 5.5 : 1); anti-3d : syn-3d = 3.2 : 1 by capillary GC.

3e: From ester 6b via acid 7b (anti : syn = 4.2 : 1); anti-3e : syn-3e = 3.4 : 1 by capillary GC.

3g: From ester 6c via acid 7c (anti : syn = 3.7 : 1); anti-3g : syn-3g = 3.4 : 1 by capillary GC.

3l: From ester 6d via acid 7d (anti : syn = 2.8 : 1); anti-3l : syn-3l = 2.8 : 1 by ^{1}H-NMR.

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