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REGIO- AND STEREOSELECTIVITY IN THE ADDITION OF METAL N,N-DIMETHYLPHENYLACETAMIDE ENOLATES TO SOME CONJUGATED CARBONYL COMPOUNDS

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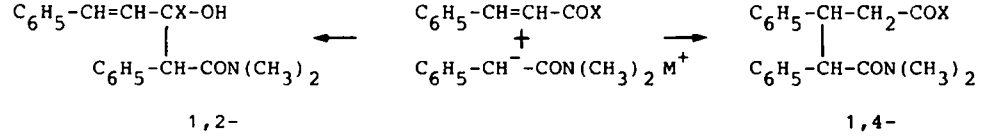
Abstract - The nucleophilic addition of lithium, sodium, potassium and bromomagnesium N,N-dimethylphenylacetamide enolates to cinnamic aldehyde, chalcone and methyl cinnamate is studied. The regioselectivity of the reaction is found to depend on the metal counterion and other reaction conditions. The stereoselectivity under kinetic and thermodynamic conditions does not depend on the metal. The reactivity of the amide-enolates is compared with the reactivity of other enolates already studied.

INTRODUCTION

The regioselectivity of the nucleophilic addition of stabilized carbanions to unsaturated carbonyl compounds has been extensively studied.[1-13] The stereoselectivity of the conjugated and the concurrent 1,2-addition, however, received scant attention.[14-18]

Dialkyl amides carboxylic acids have been rarely used as donors in the Michael reaction. Recently, we have found that the reactions of sodium N,N dialkylphenylacetamide enolates with dialkyl amides of cinnamic acid or methyl cinnamate, as well as with cinnamic aldehyde at room temperature, give only products of 1,4-addition in high yields and without complications.[19-23]

In the present work, we studied the regio- and stereoselectivity of the addition of N,N-dimethylphenylacetamide enolates to cinnamic aldehyde, chalcone and methyl cinnamate:



1,2- 1,4-

Where X = H, C_6H_5 or OCH_3,
and M = Li, Na, K or MgBr.

The electrophiles were selected according to their decreasing ability to 1,2-addition.[24] The reagents have been shown to exist in their enolate form.[25]

RESULTS AND DISCUSSION

Cinnamic aldehyde. The results from the reaction with lithium, sodium and potassium enolates are given in Table 1.

The configuration of the 1,4-addition products, i.e. the dimethyl amides of 2,3-diphenyl-5-oxovaleric acids, was determined by correlation with the 1-dimethyl amide-5-methyl ester of erythro-2,3-diphenylglutaric acid.[26] The configuration of the 1,2-addition products (the dimethyl amides of the 2,5-diphenyl-3-hydroxy-4-pentenoic acids) was assigned by comparing their IR-spectra in dilute (3.10^{-3} molar) solutions to those of the dimethyl amides of diastereomeric 2,3-diphenyl-3-hydroxypropionic acids with known configuration[27] (Fig. 1).

Table 1. Regio- and stereoselectivity of the reaction with cinnamic aldehyde.

T°C	Time	%	1,2/1,4	$E/T_{1,2}$	$E/T_{1,4}$
			Li^+		
22	5 s	92	97/3	27/73	52/48
	24 h	90	67/33	27/73	52/48
64	5 s	97	78/22	27/73	53/47
	3 h	92	0/100	-	5/95
			Na^+		
-78	1 h	67	100/0	28/72	-
-40	1 m	58	81/19	19/81	53/47
	3 h	86	0/100	-	53/47
0	5 s	61	0/100	-	52/48
64	5 s	93	0/100	-	60/40
	1 h	88	0/100	-	5/95
			K^+		
-40	1 m	5	0/100	-	52/48
22	5 s	47	0/100	-	57/43
	1 h	42	0/100	-	5/95

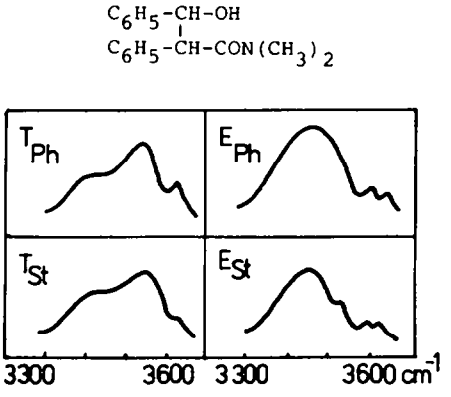


Fig. 1. IR-spectra of the diastereomeric phenyl- and styryl-hydroxyamides.

The consideration of the stable conformations in both diastereomers explains their spectral characteristics (Fig. 2). The two bands for associated hydroxyl groups (3420 and 3540 cm^{-1}) correspond to conformations T-1 and T-2, whereas the only band of the erythro-isomer (3420 cm^{-1}) is due most probably to the conformer E-2. The predominance of T-1 is supported by the ^1H NMR spectra, where the J_{threo} = 7.5 Hz and the more intensive band for hydrogen bonding should be assigned to that diequatorial conformation. In the erythro-isomers E-1 and E-2 cannot be distinguished ($J_{erythro}$ = 3-4 Hz). The maxima for the free hydroxyl groups show a higher population for E-3 than for T-3. Besides, E-3 is more populated in the styryl compound.

The assignment of the configuration is additionally supported by the fact that the erythro-isomer shows a higher R_f-value (TLC), which is in agreement with the relationship we established on more than 30 pairs of diastereomeric 1,2-disubstituted-1,2-diarylethanes.[28]

The predomination of the $threo_{1,2}$-isomer under kinetic conditions agrees with the idea of a chelate mechanism developed for aldol-type reactions.[29,30] The ratio E/T= 20/80, observed under thermodynamic conditions, cannot be interpreted, because of the shifting of the equilibrium toward the kinetically controlled 1,4-product.

The equilibrium $E/T_{1,4}$-ratio is 5/95 and can be reached at high temperatures. By studying the reaction with dialkyl amides or esters of cinnamic acid, we explained this high stereoselectivity with the stabilizing chelation in the threo-adduct.[23]

The reversibility of the 1,2-addition increases with the increase in the polarity of the medium (THF/HMPT=80/20). According to the proposed interpretation[15], this

is due to the higher HMPT solvation of the metal counterion. HMPT does not affect the stereoselectivity of the 1,2-addition.

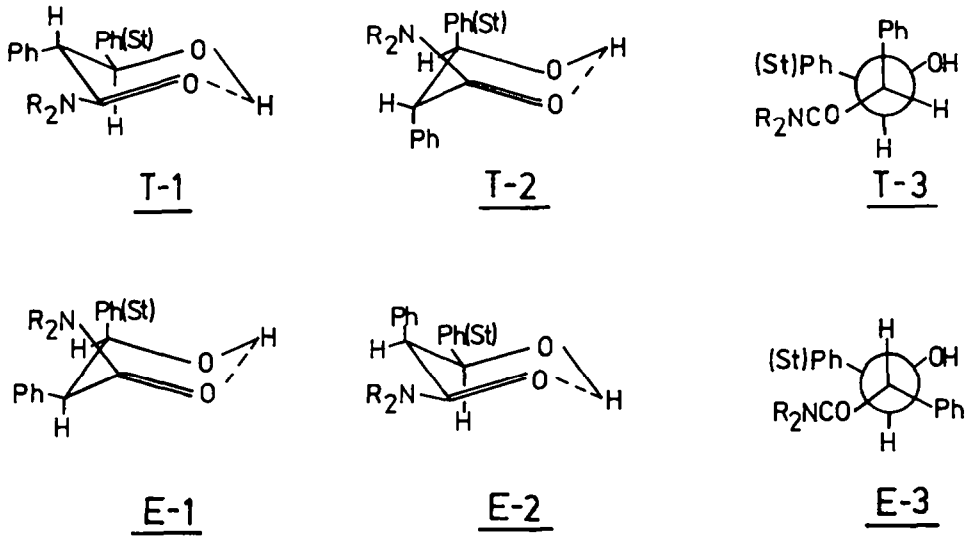


Fig. 2. Stable conformations in diastereomeric phenyl- and styryl-hydroxyamides.

Table 2. Reaction with sodium enolate in THF/HMPT = 80/20.

T°C	Time	%	1,2/1,4	E/$T_{1,2}$	E/$T_{1,4}$
-78	1 m	24	81/19	21/79	44/56
-40	1 m	35	5/95	20/80	48/52
	1 h	24	0/100	-	47/53

The reversibility of the reaction depends strongly on the nature of the metal couterion. This, one can observe an equilibrium ratio of E/T=5/95 when sodium enolate is used at -78°, whereas with lithium enolate this ratio is reached at 64° (Table 3).

In the case of bromomagnesium reagent, both 1,4- and 1,2-additions occur. At -78°, both reactions are under kinetic control with a predominance of 1,2-addition (E/T= 22/78). At 22°, 1,2-addition becomes reversible and the reaction is shifted to the kinetically controlled 1,4-adduct (E/T=47/53). Increasing the temperature makes the 1,4-addition reversible as well (E/T=10/90).

Chalcone. The reaction of this enone with lithium and sodium enolates leads regioselectively to the products of 1,4-addition: dimethyl amides of the diastereomeric 4-benzoyl-2,3-diphenylbutyric acids. The configuration of the products is determined by hydrolysis to the acids with known configuration.[31]

Table 3. Regio- and stereoselectivity of the reaction with chalcone in THF.

T°C	Time	%	1,2/1,4	E/$T_{1,2}$	E/$T_{1,4}$
			Li^+		
-78	15 s	49	0/100	-	38/62
	1 h	83	0/100	-	36/64
64	15 m	93	0/100	-	5/95
			Na^+		
-78	15 s	47	0/100	-	25/75
	1 h	63	0/100	-	7/93
			$MgBr^+$		
-78	1 h	58	58/42	22/78	45/55
22	15 s	72	24/76	54/46	43/57
	24 h	81	0/100	-	47/53
64	3 h	79	0/100	-	10/90

The IR-spectra of the 1,2-addition products in dilute solutions show a single absorption band due to strong intramolecular hydrogen bonding at the same frequen-

ce in both diastereomers and a band of very low intensity for the free OH-group. This is evidence of the fact that conformations with similar steric interactions are preferred in both stereoisomeric series (A-1 and B-1, or A-2 and B-2) and participation of a second conformation in the equilibrium is unlikely (Fig. 3).

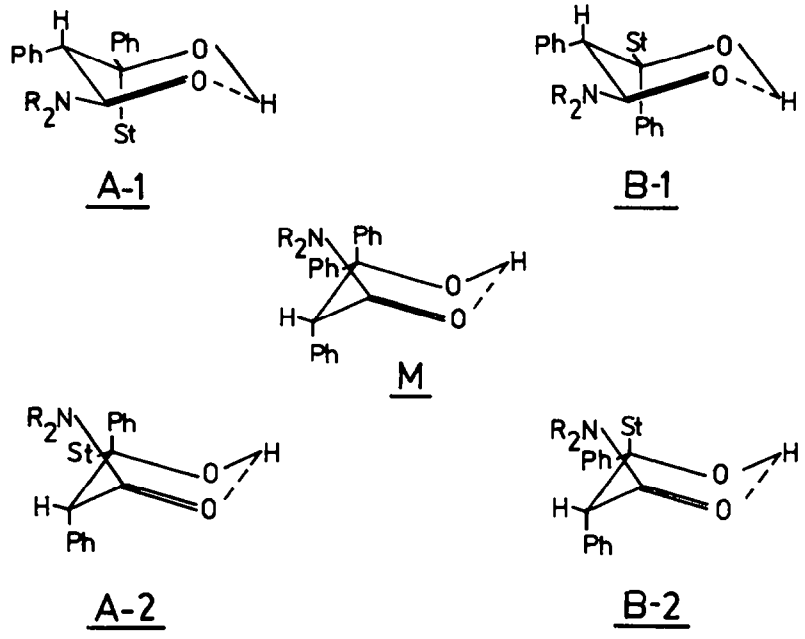


Fig. 3. Stable conformations with intramolecular hydrogen bonding.

^{1}H NMR spectra support the structure of the compounds. The CH-signal in one of the isomers is located in a weaker field and the chemical shift for the CH_3 is upfield when compared with the other isomer. In one of the isomers, the vinyl protons appear as a singlet, instead of two doublets as usual. Further spectral assignment was done by nOe experiments. The irradiation at 4.52, resp. 4.20, ppm affected the C-2 and C-3 phenyl, styryl and methyl (at 2.95, resp. 2.99, ppm) proton resonances. This observation totally eliminates conformations A-1 and B-1, in which the styryl, or phenyl, group at C-3 is axial and cannot interact with the methyne proton. The predominance of conformations A-2 and B-2 is not surprising. The $C_6H_5/N(CH_3)_2$ interaction in conformers A-1 and B-1 is similar to allylic strain forcing the phenyl group at C-2 to prefer the axial position. The nOe experiment allows the assignation of the signals at 2.95 and 2.99 to the CH_3-group closer to the methyne proton. The second "outer" group is more hindered by the axial Ph in position 3 in A-2, than by the axial St in B-2 (Dreiding molecular models). This makes it possible to assign conformation A-2 (threo-configuration*) to the isomer with a larger $\Delta\delta CH_3$-value (Table 4). The CH_3/St interaction in B-2 can explain the unusual appearance of the -CH=CH-signals in the isomer with smaller $\Delta\delta CH_3$-value.

This assignment is supported by the NMR behaviour of the 2,3,3-triphenylated compound M that we synthesized as a model. There is no doubt that the preferred conformation of this compound will not differ from the conformations A-2 and B-2 (hydrogen bonding at 3350 cm^{-1}).

* Under threo-isomers in this work we understand the isomers derived from the threo-diphenylated compound by replacement of the phenyl group or the methyne proton by a styryl group.

Table 4. Some ^{1}H NMR-parameters of the diastereomeric 1,2-adducts from the reaction with chalcone and model three-phenylated compound (δ, ppm).

Compound	CH	$N(CH_3)_2$		$\Delta\delta CH_3$	-CH=CH-	
E	4.20	2.93	2.99	0.06	6.76s	
T	4.52	2.78	2.95	0.17	6.11d	6.21d
M	4.67	2.87	3.02	0.15	-	

most probably due to the lower complexation ability of potassium and is in a good agreement with the postulated chelation in the reaction adduct.[23]

The reaction with brommagnesium enolate (higher complexation ability) leads to the products of 1,2- and 1,4-addition with predomination of the latter. The immediate 1,2-addition product - 2,5-diphenyl-5-oxo-pentenoic acid dimethyl amide was not isolated. A second addition of the starting enolate to the CO group during the reaction leads to the bis-dimethyl amides of the diastereomeric 2,4-diphenyl-3-hydroxy-3-styrylglutaric acids. Two of the three possible isomers were isolated. ^{1}H NMR spectra allow to assign to one of the isomers a meso-, and to the other a dl-, configuration (because of the equal steric environment, in a meso-compound the signals of both methyne protons and $N(CH_3)_2$-groups have the same chemical shift). The reaction with this reagent leads to the complicated reaction mixture and does not allow a precise investigation of the regio- and stereoselectivity.

Methyl cinnamate. Earlier investigations show that the sodium enolate gives with this acceptor only the 1,4-adduct.[22] Changing Na to Li does not influence the regio- and stereoselectivity (Table 5). At -78° the reaction is kinetically controlled, whereas at 22° the equilibrium ratio E/T = 5/95 is reached. When the K-enolate is used, another equilibrium ratio of 60/40 is observed. This ratio is

Table 5. Regio- and stereoselectivity of the reaction with methyl cinnamate.

T°C	Time	%	1,2/1,4	$E/T_{1,2}$	$E/T_{1,4}$
			Li^+		
-78	30 m	48	0/100	-	47/53
22	15 s	51	0/100	-	4/96
			Na^+		
-78	30 m	57	0/100	-	39/61
22*	15 s	93	0/100	-	6/94
			K^+		
22	30 m	25	0/100	-	60/40
64	5 m	27	0/100	-	58/42
			$MgBr^+$		

T°C	Time	/1,4/%	$E/T_{1,4}$	/1,2/%**	% methyl cinnamate
-78	30 m	17	31/69	17	40
22	16 h	13	25/75	5	37
64	30 m	11	10/90	8	37

*Data are taken from[22].
**As a mixture of bis-dimethyl amides of 2,4-diphenyl-3-hydroxy-5-styryl-glutaric acids.

The results obtained cannot be easily compared with the regioselectivity of the addition of other enolates because of the absence of systematic studies in the literature. Nevertheless, some conclusions can be made.

The regioselectivity of Na- and Li-amide enolates towards cinnamic aldehyde is comparable with this of arylacetonitrile derivatives.[4] No data for keto- and ester-enolates are available.

With respect to chalcone, the alkaline amide enolates are also comparable with the arylacetonitriles[3,7] (1,4-addition) and differ from the ketoenolates[18], where 1,2- and 1,4-addition was observed at low temperatures similar to the brommagnesium enolate we studied.

The comparison of the literature data with the results from the reaction of amide enolates with methyl cinnamate does not appear to provide any basis for useful conclusions at this stage.

In addition, it can be pointed out that the reaction with amide enolates proceeds without complications and can be used for stereochemical studies.

EXPERIMENTAL

M.ps. were determined on a Kofler apparatus and are uncorrected. IR-spectra were taken on a "Specord 75 IR" spectrometer. The ^{1}H NMR spectra were measured relative to TMS as internal standard on a Tesla BS 487C and Bruker WM 250 spectrometers. TLC was performed on Merck Kieselgel 60.

The sodium enolate was prepared by treatment with sodium amide.[22] The lithium enolate was made by treating the THF solution of the dimethyl amide (1 mmol in 1 ml) with an equimolar amount of t-BuLi in n-pentane at room temperature. The potassium enolate was obtained by stirring the THF solution of the amide with 1.5 moles of highly dispersed potassium for 60 min at 22°. The brommagnesium reagent was made from the Li-enolate and an equimolar amount of $MgBr_2$.

General procedure. An equimolar amount of the electrophile in 2 ml of the solvent was added with stirring under nitrogen at the corresponding temperature to the 1 mmol solution of the freshly prepared enolate in the same solvent. At the end of the reaction time, a few drop of dilute hydrochloric acid were added, the main amount of the solvent was removed under vacuum and the residue extracted with chloroform.

The E/T and 1,2/1,4 ratios were determined using preparative TLC and NMR spectroscopy (the isomers differ in the location of the signals of CHO, C_2-H and $CON(CH_3)_2$ protons). In the case where cinnamic aldehyde was used, the mixture of 1,2- and 1,4-adducts was separated in two fractions - the first with a higher R_f-value, containing the two products with erythro-configuration and the second containing both threo-isomers. On the basis of the integral intensities of the aldehyde protons in the 1,4-addition product to that of the CH=CH protons (1,2-addition), using the weight of the fractions, 1,2/1,4 and E/T ratios were determined.

Description of the products

2,5-Diphenyl-3-hydroxy-4-pentenoic acids dimethyl amides. The threo-isomer was obtained from the reaction mixture prepared at -40° in THF for 1 min after two-fold recrystallization from ethanol, m.p. 164-165°. IR (cm^{-1}, 3.10^{-3} mol/l in CCl_4): 1635 (CO), 3602 (non-bonded OH), 3540, 3442 (OH--OC). ^{1}H NMR ($CDCl_3$)δ: 7.00-7.36 (10H, m, C_6H_5), 3.73 and 3.87 (1H, d, J=8 Hz, H-2), 4.63-4.93 (1H, m, H-3), 5.83, 6.00, 6.17 and 6.25 (1H, dd, H-4), 6.41 and 6.68 (1H, d, H-5), 4.38 and 4.46 (1H, d, OH), 2.83 and 2.95 (6H, d, CH_3). Found: 4.78. $C_{19}H_{21}O_2N$ requires N 4.74%. R_f = 0.82 (ether with 5% ethanol).

The erythro-isomer was isolated from the mother liquor by TLC (ether with 5% ethanol). M.p. 134-136° (n-heptane). IR (cm^{-1}, 3.10^{-3} in CCl_4): 1634 (CO), 3606 (non-bonded OH), 3524, 3444 (OH--OC) and 3583 (OH--C_6H_5). ^{1}H NMR ($CDCl_3$)δ: 7.00-7.36 (10H, m, C_6H_5), 3.85 and 3.80 (1H, d, J=4.5 Hz, H-2), 4.80-5.06 (1H, m, H-3), 5.80, 5.90, 6.06 and 6.48 (1H, dd, H-4), 6.43 and 6.66 (1H, d, H-5), 2.78 and 2.93 (6H, d, CH_3). Found: 4.78. $C_{19}H_{21}O_2N$ requires N 4.74%. R_f = 0.82 (ether with 5% ethanol).

2,3-Diphenyl-5-oxovaleric acids dimethyl amides. The preparation and purification are already described.[26]

Threo-isomer: IR (cm^{-1}, $CHCl_3$): 1725 (CHO), 1640 (CO-amide). ^{1}H NMR ($CDCl_3$)δ: 9.63 (1H, t, CHO), 6.80-7.40 (10H, m, C_6H_5), 3.87-4.12 (2H, m, H-3 and H-2), 2.75-3.10 (8H, m, CH_3 and H-4), 2.96 (s, CH_3). M.p. 113-115° (n-heptane), R_f = 0.62 (5% ethanol in ether).

Erythro-isomer: IR (cm^{-1}, $CHCl_3$): 1725 (CHO), 1640 (CO-amide). ^{1}H NMR ($CDCl_3$)δ: 9.33 (1H, t, CHO), 7.07-7.70 (10H, m, C_6H_5), 4.02-4.25 (2H, m, H-2 and H-3), 2.80, 2.70 (6H, d, CH_3), 2.35, 2.60 (2H, m, H-4), M.p. 139-141° (benzene), R_f = 0.83 (5% ethanol in ether).

4-Benzoyl-2,3-diphenylbutyric acids dimethyl amides. The threo-isomer was isolated from the reaction mixture obtained in THF at 22° for 1 hour by recrystallization from ethanol. M.p. 207-209°. IR (cm^{-1}, $CHCl_3$): 1676 (CO ketone), 1632 (CO amide). ^{1}H NMR ($CDCl_3$)δ: 6.83-8.07 (15H, m, C_6H_5), 3.90-4.17 (2H, m, H-2 and H-3), 3.26-3.63 (2H, m, H-4), 2.90 (6H, s, CH_3). Found: N 3.92. $C_{25}H_{25}O_2N$ requires N 3.77%. R_f = 0.27 (ether/petroleum ether 1:1).

Hydrolysis of the product with HCl 1:1 in ethanol leads to the threo-4-benzoyl-2,3-diphenylbutyric acid, m.p. 185-187° (lit.[31] 185-187°).

The erythro-isomer is prepared from the reaction mixture obtained at 64° for 10 sec after separation of the threo-product by recrystallization and preparative TLC (ether/petroleum ether 1:1) of the mother liquor. M.p. 168-169° (ethanol). IR (cm^{-1}, $CHCl_3$): 1676 (CO ketone), 1632 (CO amide). ^{1}H NMR ($CDCl_3$)δ: 6.87-7.75 (15H, m, C_6H_5), 4.17-4.37 (2H, m, H-2 and H-3), 3.00-3.27 (2H, m, H-4), 2.62 and 2.82 (6H, d, CH_3). Found: N 4.06. $C_{25}H_{25}O_2N$ requires N 3.77%. R_f = 0.27 (ether/petroleum ether 1:1).

The hydrolysis of the product gives erythro-4-benzoyl-2,3-diphenylbutyric acid, m.p. 256-258° (lit.[31] 260-261°).

3-Hydroxy-2,3,5-triphenyl-4-pentenoic acids dimethyl amides. Both isomers were isolated from the reaction mixture obtained after the reaction of chalcone with bromomagnesium enolate in THF at -78° for 1 min by TLC (ether/petroleum ether 1:1).

Threo-isomer: M.p. 133-135° (ethanol), R_f = 0.48. IR (cm^{-1}, 3.10^{-3} in CCl_4): 3606 (nonbonded OH), 3334 (OH--OC). ^{1}H NMR ($CDCl_3$)δ: 7.07-7.63 (15H, m, C_6H_5), 6.90 (1H, s, OH), 6.18, 6.24 (1H, d, H-5), 6.09, 6.15 (1H, d, H-4), 4.52 (1H, s, H-2), 2.78, 2.95 (6H, d, CH_3). Differential spectrum after irradiation at 4.52 ppm: 2.95 (s, CH_3), 6.09, 6.15 (d, H-4), 6.18, 6.24 (d, H-5), 7.42, 7.45 (d, o-H), 7.59, 7.62 (d, o-H). Found: C 80.42, H 6.54. $C_{25}H_{25}O_2N$ requires C 80.86%, H 6.73%.

Erythro-isomer: M.p. 144-146° (ethanol), R_f = 0.59. IR (cm^{-1}, 3.10^{-3} in CCl_4): 3600 (nonbonded OH), 3330 (OH--OC). ^1H NMR ($CDCl_3$)δ: 7.13 (1H, s, OH), 6.97-7.46 (15H, m, C_6H_5), 6.78 (2H, s, CH=CH), 4.20 (1H, s, H-2), 2.93, 2.99 (6H, d, CH_3). Differential spectrum after irradiation at 4.20 ppm: 2.99 (s, CH_3), 6.76 (s, CH=CH), 6.99, 7.02 (d, o-H), 7.23, 7.26 (d, o-H). Found: C 80.51, H 6.92. $C_{25}H_{25}O_2N$ requires C 80.86%, H 6.73%.

3-Hydroxy-2,3,3-triphenylpropionic acid dimethyl amide. The solution (1 ml) of bromomagnesium enolate was added to the stirred mixture of 0.180 g (1 mmol) benzophenone in 2 ml THF and 0.4 ml of a 2.5 molar solution of $MgBr_2$ in ether and the viscous product was separated after 15 min and solidified by acidification (HCl) and washing with 5 ml H_2O and 5 ml ether. Recrystallization from $CHCl_3$ leads to the pure product with m.p. 179-180° (38%). IR (cm^{-1}, 3.10^{-3} in CCl_4): 3350 (OH--OC), no nonbonded OH. ^1H NMR ($CDCl_3$)δ: 7.09 (1H, s, OH), 6.62-7.59 (16H, m, C_6H_5 + OH), 4.67 (1H, s, CH), 2.87, 3.02 (6H, d, CH_3). Found: C 79.40, H 6.81. $C_{23}H_{23}O_2N$ requires C 79.97%, H 6.71%.

Reaction of the bromomagnesium enolate with methyl cinnamate. The reaction mixture obtained at -78° for 60 sec was separated by TLC (ether) in three fractions. The first (R_f = 0.52) gives after recrystallization from ethanol dl-2,4-diphenyl-3-hydroxy-3-styrylglutaric acid bisidimethyl amide with m.p. 198-200°. IR (cm^{-1}, 3.10^{-3} in CCl_4): 3386, 3236 broad (H bonded OH intramolecular). ^1H NMR ($CDCl_3$)δ: 7.00-7.60 (15H, m, C_6H_5), 5.77, 6.83 (1H, d, CH=), 5.60, 5.66 (1H, d, =CH), 6.14 (1H, s, OH), 4.73 (1H, s) and 4.47 (1H, s)(H-2 and H-4), 2.90, 2.96, 3.00 and 3.02 (12H, 2d, CH_3). Found: N 6.24. $C_{29}H_{32}O_3N_2$ requires N 6.14%.

The second fraction (R_f = 0.73) affords on recrystallization 1-dimethyl amide-5-methyl ester of threo-2,3-diphenylglutaric acid.[22]

The fraction with R_f = 0.90 was purified by chromatography once more (three-fold elution with ether/petroleum ether 1:1). From the fraction with R_f = 0.60 was isolated the pure 1-dimethyl amide-5-methyl ester of erythro-2,3-diphenylglutaric acid.[22] The second fraction (R_f = 0.43) led to the isomeric meso-2,4-diphenyl-3-hydroxy-3-styrylglutaric acid bis dimethyl amide, m.p. 174-176° (ethanol). IR (cm^{-1}, 3.10^{-3} in CCl_4): 3248, 3174 (H bonded OH, intramolecular). ^1H NMR ($CDCl_3$)δ: 7.00-7.60 (15H, m, C_6H_5), 8.26 (1H, s, OH), 6.51, 6.45 (1H, d, CH=), 6.24, 6.30 (1H, d, =CH), 4.75 (2H, s, H-2 and H-4), 2.68, 2.89 (12H, d, CH_3). Found: N 6.28. $C_{29}H_{32}O_3N_2$ requires N 6.14%.

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