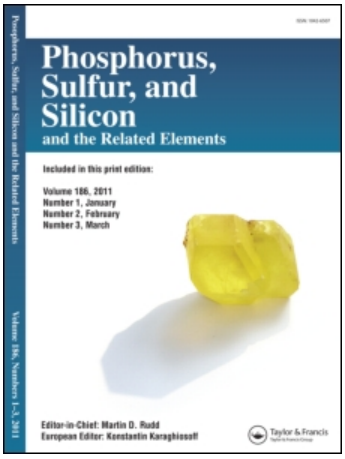

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N,N-DIALKYLTHIOAMIDES IN THE MICHAEL ADDITION TO CONJUGATE CARBONYL COMPOUNDS, REGIOSELECTIVITY, STEREOCHEMISTRY AND MECHANISM

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The regio- and diastereoselectivity of the addition of *N,N*-dialkylphenylthioacetamide enolates to some conjugate carbonyl compounds are studied. The results are compared with oxoanalogs and the differences are rationalized in terms of specific behaviour of sulfur. General trend to 1,4-addition is demonstrated. The stereochemistry is correlated with the cyclic transition state taking into account the ground state conformation preferred by the acceptor.

Key words: *N,N*-dialkylthioamides; Michael reaction; regioselectivity; diastereoselectivity; transition state.

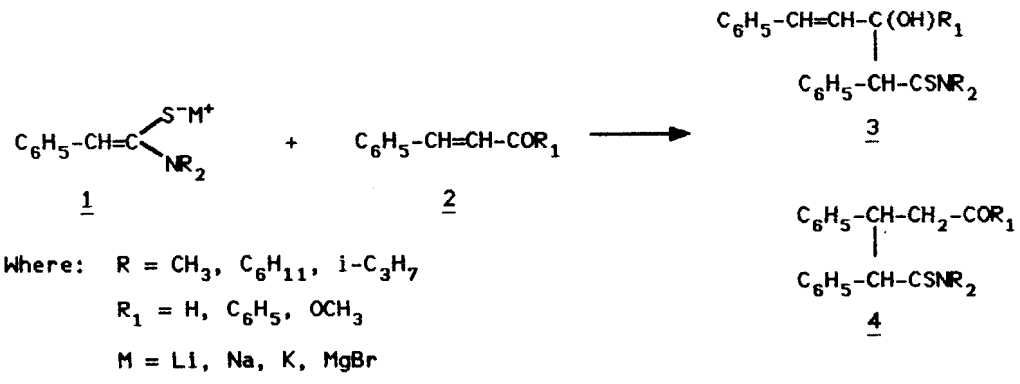
INTRODUCTION

The regio- and stereoselectivity of the addition of metal reagents to conjugate carbonyl compounds is of current interest.[1] In our previous works the behaviour of *N,N*-dialkylphenylacetamide enolates towards some ambidentate electrophiles had been explored.[2,3,4] The steric course of both 1,2- and 1,4-addition had been interpreted in terms of a cyclic transition state hypothesis.[2,4] Some interesting observations about the factors dictating kinetic and thermodynamic diastereofacial selectivity have been done.[4,5,6]

It was of common interest to study the addition of the corresponding *N,N*-dialkylthioamides and to compare the regio- and stereoselectivity of the reaction with those of the oxoanalogs studied before.

Thioamides had been used as Michael donors in a few cases.[7–9] A detailed study of the regio- and stereoselectivity of the Michael addition to α,β-unsaturated ketones is represented by C. Heathcock.[7] Although chalkone had been used in the reaction with thioamides, products of 1,2-addition had not been found and the stereochemistry of the conjugate reaction had not been quantified.[8] To our knowledge there is no data about the addition of thioamides to conjugate aldehydes and esters.

In this paper we study the regio- and stereoselectivity of the addition of *N,N*-dialkylthiophenylacetamide enolates 1 to some α,β-unsaturated carbonyl compounds 2 leading to 1,2- and /or/ 1,4-adducts 3, resp. 4 with two adjacent asymmetric centra:



An attempt is made to explain the data obtained in sence of regularities found before.

Thioamides are more acidic than the oxoanalogs and can be easily converted into enolates using various base/solvent combinations. According to the literature enthiolates possess in general *Z*-configuration in very high geometric purity.[10,11]

CONFIGURATIONAL ASSIGNMENT

The configuration of the *N,N*-dimethylamides of the diastereosiomeric 2,3-diphenyl-5-oxo-thiovaleric acids 4a,4b (Table V) was assigned using the correlation obtained for the corresponding oxoanalogs between the location of the CHO signals and the stereostructure.[3] Erythro configuration was attributed to the isomers with up-field location. The difference observed was used for the analysis of the reaction mixtures.

The configuration of the dimethylamides of the diastereoisomeric 4-benzoyl- and 4-methoxycarbonyl-2,3-diphenyl-thiobutyric acids 4c–4g (Table IV) were correlated with the corresponding oxoderivatives[12] by stereoselective reduction to aminoalcohols.

We did not succeed in making the same correlation in the case of 2,5-diphenyl-3-hydroxy-4-pententhioic acid dimethylamides 3a–3b (Table IV). The configurational assignment was based on the similarity of their ^{1}H NMR spectra with those in the oxo-series.[3,4] Thus, *E* stereostructure was attributed to the isomer with downfield shifting of the H-4 and H-5 protons.

RESULTS AND DISCUSSION

The results obtained are summarized in Tables I–III. The data available for the oxoanalogs marked by an asterisk (*) are cited for comparison. Physical, analytical and ^{1}H NMR data for compounds 3 and 4 are given in Tables IV and V.

According to Pearson's theory about "hard and soft acids and bases"[13] thioamides are softer nucleophiles than oxoamides and have therefore higher trend to 1,4 addition.[14,15] This trend is clearly demonstrated in the reaction of the lithium

TABLE I

Addition to cinnamic aldehyde (R = H) in THF

Example	*R*	*M+*	*T°C*	*Time*	*%*	*1.2/1.4*	$E/T_{1,2}$	$E/T_{1,4}$
1*	CH_3	Li	-40	1 min	85	100/0	27/73	-
			22	24 h	90	67/33	27/73	52/48
1	CH_3	Li	-78	60 min	63	46/54	12/88	52/48
			22	60 min	72	0/100	-	61/39
2	CH_3	MgBr	-78	60 min	80	100/0	46/54	-
			22	60 min	82	100/0	18/82	-
3	$i\text{-}C_3H_7$	Li	-40	30 min	70	37/63	48/52	67/33
			22	60 min	75	5/95	-	73/27
4	$i\text{-}C_3H_7$	MgBr	-40	30 min	75	100/0	47/53	-
			22	60 min	75	100/0	23/77	-

TABLE II

Addition to chalcone (R_1 = Ph) in THF

Example	R	M+	*T°C*	*Time*	*%*	*1,2/1,4*	$E/T_{1,2}$	$E/T_{1,4}$
1*	CH_3	Li	-78	15 sec	49	0/100	-	38/62
			64	15 min	93	0/100	-	5/95
1	CH_3	Li	-40	60 sec	89	0/100	-	83/17
			22	3 h	68	0/100	-	40/60
2*	CH_3	MgBr	-78	1 h	58	58/42	22/78	45/55
2	CH_3	MgBr	-78	d o e s	n o t	r e a c t		
			-40	60 sec	38	0/100	-	58/42
			22	1 h	30	0/100	-	56/44
3*	$i\text{-}C_3H_7$	Li	-40	5 min	65	0/100	-	59/41
3	$i\text{-}C_3H_7$	Li	-78	60 min	60	0/100	-	81/19
			22	60 min	55	0/100	-	45/55
4	$i\text{-}C_3H_7$	MgBr	-78	60 sec	43	0/100	-	50/50
			22	1 h	55	0/100	-	52/48

thiodimethylphenylacetamide enolate (compare 1 and 1*) to cinnamic aldehyde. At low temperature lithium reagents exhibit mixed regioselectivity (see 1 and 3) and both 1,2- and 1,4-additions studied proceed under kinetic control. The 1,4-diastereoselectivity is as poor as in the case of the oxoanalog (see 1*). Appreciable increase of the erythro isomer (E/T = 67/33) is observed with the bulkier thio-

diisopropylamide. At 22°C the reaction becomes 1,4-regioselective and reversible with moderate predominance of the erythro form.

The use of bromomagnesium reagents reverses the regioselectivity course in favour of 1,2-addition (compare 1 and 2, 3 and 4). Obviously the change of the metal counterion strongly influences the "hardness" of the enolates and consequently the discrimination between aldol and conjugate reactions. The addition is 1,2-regioselective up to 22°C. Dependence of the kinetic 1,2-diastereoselectivity on the metal counterion is observed (compare 1 and 2). At higher temperature (conditions of reversibility) the threo isomer predominates.

The addition of the lithium and bromomagnesium reagents of the thioamides examined to chalcone occurs 1,4-regioselectively while in the oxo series 1,2-addition also takes place (see 2*). With the lithium thioenolates the stereoselectivity is good in favour of the erythro isomer and its amount increases considerably in comparison with the oxoamides (compare 1 and 1*, 3 and 3*). The reaction becomes reversible at 22°C and the thermodynamic ratio is E/T = 40/60. With the bromomagnesium reagents the addition is kinetically controlled and nonselective in the hole temperature interval (E/T about 1:1) for both thio- and oxo-series.

Lithium and sodium enthiolates failed to react with methylcinnamate in contrast to the corresponding enolates. Their decreased nucleophilicity is obviously connected with stronger cation-anion association, caused by the change of oxygen with sulfur.[16] The ion-pairing can be decreased either by increasing the dissociating power and the basicity of the solvent (HMPT) or by using species with greater ionic radia. Actually, the use of THF/K^+ or HMPT/Na^+ results in a successful interaction.

The addition of the thioenolates occurs 1,4-regioselectively. The yield varies

TABLE III

Addition to methyl cynamate (R_1 = OCH_3)

Example	R	M+	Solvent	T°C	Time	%	E/T$_{1,4}$
1*	CH_3	K	THF	-78	30 min	78	68/32
				22	15 sec	48	11/89
1	CH_3	K	THF	-40	30 min	23	100/0
				22	30 min	28	58/42
2	CH_3	Na	HMPT	22	60 min	56	50/50
3*	C_6H_{11}	K	THF	-40	30 min	68	68/32
				64	60 sec	80	25/75
3	C_6H_{11}	K	THF	-40	does not react		
				0	15 min	18	82/18
				22	30 min	28	60/40
4	C_6H_{11}	Na	HMPT	22	2 h	23	70/30
5	i-C_3H_7	Na	HMPT	22	2 h	18	73/27

TABLE IV

Physical and ^1H NMR data for the adducts 3

Compound and configuration	R	R_1	Mp °C (solvent)	R_f [a] (Et_2O : LP ratio)	δ
Erythro 3a	CH_3	H	not isolated[b]	0.26 (3 : 2)	3.12, 3.46(d, 6H, CH_3), 4.05, 4.06(d, 1H, H-2, J=2.18 Hz), 5.12-5.20 (m, 1H, H-3), 5.36(br, 1H, OH), 6.07, 6.10, 6.14, 6.16(dd, 1H, H-4), 6.52, 6.58(d, 1H, H-5, J=16.15 Hz), 7.14-7.53(m, 10H, C_6H_5).
Threo 3a	CH_3	H	138-140 (EtOH)	0.21 (3 : 2)	3.23, 3.49(d, 6H, CH_3), 3.88, 3.91(d, 1H, H-2, J= 8.81 Hz), 4.5(br, 1H, OH), 5.09, 5.11, 5.12, 5.15 (dd, 1H, H-3), 6.43, 6.50(d, 1H, H-5, J=16 Hz), 7.2-7.8(m, 10H, C_6H_5).
Erythro 3b	i-C_3H_7	H	not isolated[b]	0.47 (1 : 1)	3.19-3.42(br, 1H, $CH(CH_3)_2$), 4.21-4.37(m, 1H, $CH(CH_3)_2$), 5.19-5.30(m, 1H, H-3), 6.26, 6.24, 6.20, 6.16(dd, 1H, H-4), 6.54, 6.60(d, 1H, H-5), 7.10-7.60(m, 10H, C_6H_5).
Threo 3b	i-C_3H_7	H	140-142 (EtOH)	0.53 (1 : 1)	0.5-1.9(m, 12H, $CH(CH_3)_2$), 3.61-3.90(br, 2H, H-2+ $CH(CH_3)_2$), 4.50-4.70(br, 1H, $CH(CH_3)_2$), 4.82(br, 1H, OH), 5.10, 5.17, 5.13(t, 1H, H-3), 6.03, 6.09 (d, 1H, H-4), 6.54, 6.60(d, 1H, H-5, J=15.65 Hz), 7.1-7.6(m, 10H, C_6H_5).

[a] LP = Light petroleum (b.p. 40–70°C).

[b] ^1H NMR data are taken from diastereoisomeric mixtures, obtained by means of preparative TLC.

TABLE V

Physical and ^{1}H NMR data for the adducts 4

Compound and configuration	R	R_1	Mp °C (solvent)	R_f (Et_2O : LP ratio)	δ
Erythro 4a	CH_3	H	oil	0.31 (3 : 2)	2.42-2.54(m, 2H, H-4), 3.23, 3.26(d, 6H, CH_3), 4.51-4.63(m, 2H, H-2+H-3), 7.00-7.69(m, 10H, C_6H_5), 9.33(t, 1H, CHO).
Threo 4a	CH_3	H	oil	0.21 (3 : 2)	2.75-2.83(m, 2H, H-4), 3.38, 3.49(d, 6H, CH_3), 4.23, 4.27(d, 1H, H-2, J=11 Hz), 4.36-4.45(m, 1H, H-3), 6.93-7.36(m, 10H, C_6H_5), 9.56(t, 1H, CHO).
Erythro 4b	i-C_3H_7	H	162-164 (EtOH)	0.49 (1 : 1)	0.94-1.56(m, 12H, $CH(CH_3)_2$), 2.47-2.53(m, 2H, H-4), 3.60-3.75(br, 1H, $CH(CH_3)_2$), 4.36, 4.40(d, 1H, H-2, J=10 Hz), 4.72-4.82(m, 2H, H-3+$CH(CH_3)_2$), 7.13-7.69(m, 10H, C_6H_5), 9.33(t, 1H, CHO).
Threo 4b	i-C_3H_7	H	not isolated	0.46 (1 : 1)	9.56(t, 1H, CHO).[a]
Erythro 4c	CH_3	C_6H_5	185-187 (EtOH)	0.35 (3 : 2)	2.93-3.15(m, 2H, H-4), 3.21, 3.31(d, 6H, CH_3), 4.64-4.72(m, 1H, H-3), 4.75, 4.79(d, 1H, H-2, J= 10.5 Hz), 7.07-7.74(m, 15H, C_6H_5).
Threo 4c	CH_3	C_6H_5	158-160 (EtOH)	0.27 (3 : 2)	3.20-3.37(m, 1H, H-4), 3.45, 3.51(d, 6H, CH_3), 3.91, 3.92, 3.97, 3.98(dd, 1H, H-4), 4.42-4.52(m, 2H, H-2+H-3), 6.90-7.94(m, 15H, C_6H_5).
Erythro 4d	i-C_3H_7	C_6H_5	160-162 (EtOH)	0.52 (1 : 1)	0.92-1.57(m, 12H, $CH(CH_3)_2$), 3.00-3.21(m, 2H, H-4), 3.50-3.85(br, 1H, $CH(CH_3)_2$), 4.06-4.18(m, 1H, H-3), 4.24-4.41(m, 2H, H-2+$CH(CH_3)_2$), 7.00-7.81(m, 15H, C_6H_5).
Threo 4d	i-C_3H_7	C_6H_5	167-169 (EtOH)	0.47 (1 : 1)	0.77-1.95(m, 12H, $CH(CH_3)_2$), 3.08-3.36(m, 1H, H-4), 3.78-5.00(br, overlaped signals for H-4+H-2+H-3+ $CH(CH_3)_2$), 6.75-8.00(m, 15H, C_6H_5).

Erythro 4e	CH_3	OCH_3	150-152 EtOH	0.35 (2 : 1)	2.3-2.5(m, 2H, H-4), 3.20, 3.28(d, 6H, CH_3), 3.83 (s, 3H, $COOCH_3$), 4.42-4.52(m, 1H, H-3), 4.60-4.64 (d, 1H, H-2, J=10.6 Hz), 7.16-7.71(m, 10H, C_6H_5).
Threo 4e	CH_3	OCH_3	137-139 (EtOH)	0.29 (2 : 1)	2.73, 2.77, 2.79, 2.83(dd, 1H, H-4), 3.44, 3.49 (d, 9H, CH_3+$COOCH_3$), 4.26-4.36(m, 1H, H-3), 4.40-4.44(d, 1H, H-2, J=11,1 Hz), 6.95-7.32(m, 10H, C_6H_5).
Erythro 4f	C_6H_{11}	OCH_3	107-110 (EtOH)	0.45 (1 : 3)	1.08-1.84(m, 18H, cyclohexyl-H), 2.39-2.49(m, 2H, H-4), 2.88-3.13(br, 1H, cyclohexyl-H), 3.37(s, 3H, $COOCH_3$), 4.36-4.47(m, 2H, H-2+cyclohexyl-H), 4.55-4.61(m, 1H, H-3), 7.14-7.71(m, 10H, C_6H_5).
Threo 4f	C_6H_{11}	OCH_3	140-142 (EtOH)	0.51 (1 : 3)	0.87-2.14(m, 18H, cyclohexyl-H), 2,65-2,75(m, 1H, H-4), 3.26-3.83(m, 2H, H-4+cyclohexyl-H), 3.45(s, 3H, $COOCH_3$), 4.08-4.49(m, 3H, H-2+H-3+cyclohexyl-H), 6.99-7.28(m, 10H, C_6H_5).
Erythro 4g	C_3H_7	OCH_3	160-162 (EtOH)	0.48 (1 : 1)	0.9-1.69(m, 12H, $CH(CH_3)_2$), 2.34-2.53(m, 2H, H-4), 3.38(s, 3H, $COOCH_3$), 3.67-3.74(m, 1H, $CH(CH_3)_2$), 4.44, 4.48(d, 1H, H-2, J=10.2 Hz), 4.56-4.66(m, 1H, H-3), 4.68-4.93(br, 1H, $CH(CH_3)_2$), 7.11-7.72 (m, 10H, C_6H_5).
Threo 4g	C_3H_7	OCH_3	152-154 (EtOH)	0.53 (1 : 1)	0.69-1.90(m, 12H, $CH(CH_3)_2$), 2.67, 2.71, 2.73, 2.77(dd, 1H, H-4), 3.26-3.36(m, 1H, H-4), 3.47(s, 3H, $COOCH_3$), 3.77-3.95(br, 1H, $CH(CH_3)_2$), 4.11-4.28(br, 1H, H-3), 4.28-4.45(br, 1H, H-2), 4.75-4.95(br, 1H, $CH(CH_3)_2$), 7.00-7.27(m, 10H, C_6H_5).

[a] The other signals are not referred as always 1,2 additional products present in the reaction mixture.

from good to poor depending on the relative size of the dialkylamino group. The reaction with potassium enolates under kinetic conditions (low temperature) is highly erythro selective (see 1 and 3); in the case 3 interference of reversibility seems quite probable. Analogically to chalkone, increase of the erythro proportion in comparison with the oxoanalogs is registrated (compare 1 and 1*, 3 and 3*).

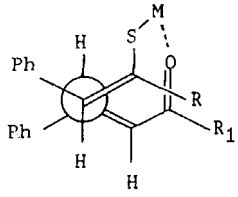
Under thermodynamic conditions (22°C) the diastereoselectivity is low in contrast to the oxoamides where good threo preference is observed (compare 1 and 1*, 3 and 3*).

Having in mind some theoretical consideration[16] as well as our previous results,[17,19] to improve the reaction yields we carried out the syntheses in HMPT. Unfortunately the results were not satisfactory, excluding example 2. The stereochemical ratios obtained reflect most probably the thermodynamic stability of the reaction adducts.

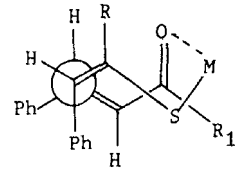
The analysis of experimental data allows several general conclusions to be drawn:

— Thioamides have a definite trend to 1,4-versus 1,2-addition, which may be changed by the variation of the metal counterion in the reagent.
— The stereoselectivity at both 1,2- and 1,4-levels depends on the metal used and the substituents in the reactants.
— Contrary to the oxoamides high thermodynamic threo-preference due to a stabilizing chelation[2] is not observed.

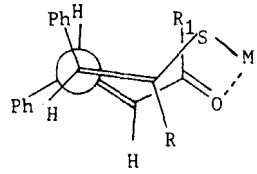
To explain the stereochemistry of the 1,4-addition we consider transition state models *T*- and *E*-postulated before.[2,4]



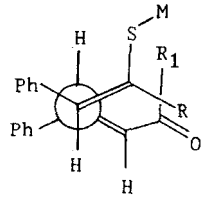
T-1



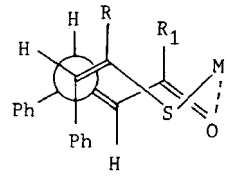
E-2



T-3'



T-3



E-4

The following reasons are taken into account:

(a) *Z*-configuration of the thioamide enolates;
(b) *E*-configuration of the electrophile;
(c) *s*-cis conformation of the acceptor's carbonyl group when R = Ph or OCH_3 and *s*-trans when R = H.[18]

In the reaction of chalcone and methyl cinnamate (R_1 = Ph, OCH_3) transition states *T*-1 and *E*-2 are under consideration. The steric interaction R/R_1 will favour the obtaining of erythro isomer. The increased erythro selectivity in comparison to the O-analogs is in agreement with Heathcock's generalization that the use of thioamides and/or alkali metals with greater ionic radia will favour transition state *E*-2 over *T*-1 because of the more convenient mode of chelation.[7]

With bromomagnesium reagents the additional steric requirements of the bromomagnesium cation must be taken into account. It is large enough coordination in *T*-1 to be preferred, thus decreasing the relative amount of the erythro isomer.

When R_1 = H (cinnamic aldehyde) the increase of the *E*-diastereoselectivity parallel to the bulk of the dialkylamino group can be explained only if *s*-trans conformation of the acceptor's carbonyl group is taken into consideration in transition states *T*-3 and *E*-4; in geometry *T*-3 coordination is impossible. It is obvious that with bulkier amides transition state *E*-4 will be preferred. To our knowledge this is the first evidence in support of correlation between electrophile's carbonyl group conformation and stereochemical outcome of the Michael reaction.[1]

As a result of the present investigation the preparative scope of the Michael reaction with thioamides is extended. The behaviour of the thioamides examined correspond to the specific character of the sulfur atom in coordination and transition states determining the stereochemistry of the reaction.

EXPERIMENTAL

The syntheses were carried out in anhydrous conditions and freshly distilled over $LiAlH_4$ THF under dry argon atmosphere. The ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer with TMS as an internal standard and using $CDCl_3$ as a solvent. Mps. were measured on a Kofler apparatus and are uncorrected. The qualitative TLC investigations were performed on Kisselgel Merk 60 F_{254}. *E/T* ratios were determined by ^1H NMR using the differences in location of signals for erythro and threo forms.

Preparation of the thioamides $PhCH_2CSNR_2$. The thioamides were prepared from the corresponding amides by using Lawesson's reagent[19] in dry benzene. Yields, mps. and solvent for recristalization are as follows: $R = CH_3$, 73%, 76–78°C (C_2H_5OH); $R = C_6H_{11}$, 67%, 109–111°C (C_2H_5OH); $R = i - C_3H_7$, 45%, 101–103°C (Et_2O).

Enolization and synthesis. General procedure. Enolization: The lithium enolates were generated by using LDA at 20°C ($R = CH_3$) or 1.6 M BuLi in hexane ($R = C_6H_{11}$, $i - C_3H_7$) at 0°C. Thus, 1 mmol of the thioamide dissolved in 1 ml THF was added dropwise to 1.1 mmol of the metalating agent in 1 ml THF and the reaction mixture was kept at stirring for 15 min.

The bromomagnesium enolates were prepared from lithium enolates by exchange with equimolar quantity of $MgBr_2$.

The potassium enolates were prepared using 1.5 mmol of KH at boiling for 15 min. when $R = CH_3$ and 30 min. when $R = C_6H_{11}$.

Synthesis: 1 mmol of the electrophile in 1 ml of the solvent were added at stirring to 1 mmol of the metal reagent at the desired temperature. At the end of the reaction time the mixture was hydrolized, the solvent was partially removed under vacuum and the residue was extracted with $CHCl_3$. After drying and evaporation of the solvent the reaction yields were determined by means of preparative TLC. The syntheses in HMPT in the presence of $NaNH_2$ were performed as one stage reaction and the mixtures were worked up according to the method described in Reference 17.

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