New Diastereoselective Method for Constructing a Carbon Chain by Conversion of *N,N'*-Dialkyl-*N,N'*-Diacylhydrazines to *threo*-1,2-Dicarboxylic Acid Derivatives

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A diastereoselective method is described for constructing a carbon chain by conversion of *N,N'*-dialkyl-*N,N'*-diacylhydrazines (**1a—f**) to dialkyldiamides of *threo*-1,2-dicarboxylic acids (**3a—f**).

[3,3] Sigmatropic rearrangements of neutral molecules are extensively used in organic chemistry,[1] as are [3,3] sigmatropic rearrangements of anions, *e.g.* carboxylic acid monoenolates (Carrol and Ireland–Claisen reactions,[2] which are diastereoselective methods of constructing a carbon chain) and *N*-aryl- *N'*-acylhydrazine monenolates (Brunner's reaction,[3] used to synthesize 2-oxy-indoles). However, the [3,3] sigmatropic rearrangements of dienolates have not been reported.

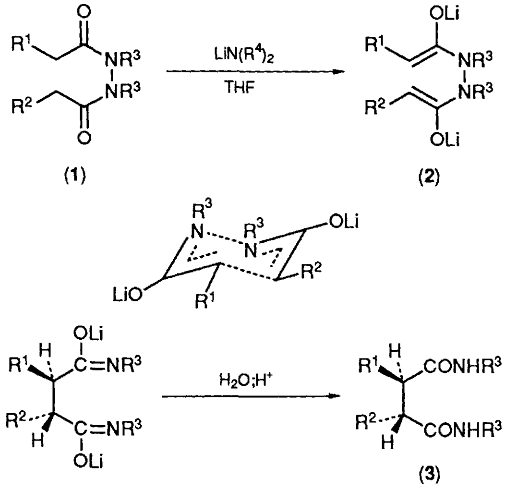
We have discovered a new diastereoselective reaction that allows one to convert *N,N'*-dialkyl-*N,N'*-diacyl-hydrazines into *threo*-1,2-dicarboxylic acid dialkyl diamides. This reaction proceeds as a [3,3] sigmatropic rearrangement *via* dienolate formation and leads to cleavage of the nitrogen–nitrogen bond yielding a new carbon–carbon bond.

Dienolates (**2a—f**) were generated from compounds (**1a—f**) by the action of strong bases such as lithium bis(trimethyl-

Table 1. Rearrangement of *N,N'*-dialkyl-*N,N'*-diacylhydrazines (**1**) to dialkyldiamides (**3**) of *threo*-1,2-dicarboxylic acid.[a]

Compound	R^1	R^2	R^3	*Threo*: *erythro* mol. ratio[b]	Yield of (**3**) (%)
a	Ph	Ph	Me	7 : 3	70
b	Ph	Ph	Pr^i	1 : 0	87
c	1-Np[e]	Np	Me	1 : 0	75
d	$PhCH_2$	$PhCH_2$	Me	1 : 0[c]	20
e	1-Np	H	Me	—	67[d]
f	1-Np	Me	Me	1 : 0	71[d]

[a] All new compounds have been fully characterized by IR, NMR, MS, and elemental analysis. [b] From NMR data. [c] With hexamethylphosphoric triamide as co-solvent. [d] Rearrangement occurs on heating at 66 °C. [e] 1-Np = 1-naphthyl.



Scheme 1. R^4 = $SiMe_3$ or Pr^i; see Table 1 for other substituents.

silyl)amide or lithium di-isopropylamide.† The overall yields of the amides (**3a—f**), obtained following acidification are in Table 1. The results of the rearrangement are the same irrespective of the base.

The diastereoselectivity of a [3,3] sigmatropic rearrangement is determined by two factors: the configuration of the enolates (**2a—f**) and the conformation of the transition state. It is known that the *Z*-configuration is more stable for amide enolates[4] and [3,3] sigmatropic rearrangements proceed primarily through a 'chair' transition state.[1] These two factors are responsible for the diastereoselective pattern of the reaction.

Thus, we have developed a convenient preparative diastereoselective method to obtain *threo*-1,2-dicarboxylic acids derivatives.

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† In a typical experiment, the *N,N'*-dialkyl-*N,N'*-diacylhydrazine (**1a—f**) (2 mmol) was added under argon to $LiN(SiMe_3)_2$ (5 mmol) in tetrahydrofuran at −78 °C. The mixture was stirred for 20 min at the same temperature and then set aside for 60 min at 25 °C. 2 M HCl was added to pH 7. The precipitate was filtered off and recrystallised.