in the *trans* complex and/or to the rate of an hypothetical intramolecular *cis-trans* isomerisation. The same behaviour is found in the $SnCl_4$–Me_2O system, but with faster exchange rates.

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69. The Preparation of *trans*-N-Acyl, N-alkyl-1-amino-1,3-butadienes

Preliminary Communication

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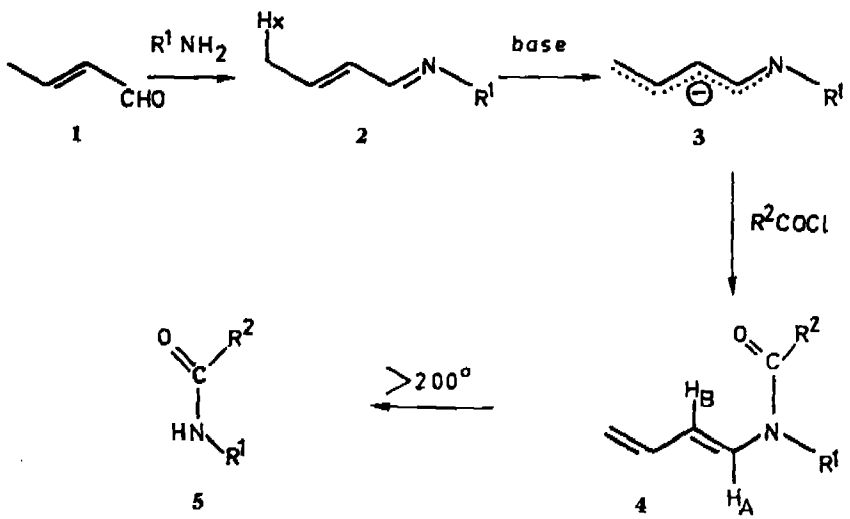
(24. I. 75)

Zusammenfassung. In der vorliegenden Mitteilung wird erstmals ein Zugang zu *trans*-N-Acyl, N-alkyl-1-amino-1,3-butadienen **4**, sowie zu *trans*-N-Acyl, N-aryl-1-amino-1,3-butadienen **4** beschrieben. Deprotonierung von N-substituierten 1-Imino-2-butenen **2** führt vermutlich zu den nicht isolierten delokalisierten Anionen **3**, die anschliessend regioselektiv am Stickstoffatom acyliert werden.

In order to achieve the stereocontrolled synthesis of substituted decahydro quinolines [1] a general approach to *trans*-N-acyl, N-alkyl-1-amino-1,3-butadienes[1])

Scheme



[1]) A multi step preparation of an endocyclic N-acyl-1-amino-4-cyano-1,3-butadiene has been described in connection with the synthesis of anthramycin [2].

Table 1. trans-*N-Acyl-1-amino-1,3-butadienes: Yields and Spectral Data*

Dienamide **4**	reaction conditions[3])	dist. (bath) °C/Torr	isolated yield	^{1}H-NMR. ($CDCl_3$) δH_A(ppm),	J_{AB}(Hz)	IR. (film) ν_{max}(cm^{-1})	UV. (MeOH) λ_{max}(nm)/log ε
$R^1 = (CH_2)_3CH=CH_2$ $R^2 = OCH_3$	a b	100/0.2	65% 36%	7.06	15	1720, 1648	257.5/4.28
$R^1 = (CH_2)_3CH=CH_2$ $R^2 = OC_6H_5$	a	140/0.1	61%	not visible		1720, 1643	208.0/3.99 258.0/4.50
$R^1 = (CH_2)_3CH=CH_2$ $R^2 = CH_3$	a	130/0.1	57%	6,68	14,5	1676, 1638	266.5/4.36
$R^1 = (CH_2)_2C(H)=C(CH_3)H$ $R^2 = OCH_3$	b	125/0.15	48%	7.17	15	1721, 1648	258.0/4.32
$R^1 = (CH_2)_2CH=CH_2$ $R^2 = OCH_3$	a	125/0.2	62%	7.09	14	1718, 1645	257.0/4.32
R^1 = cyclohexyl $R^2 = OCH_3$	a	80/0.1 m.p. 38–40°	41%	6.79	13	1720, 1652	258.0/4.43
$R^1 = (CH_2)_5CH_3$ $R^2 = OCH_3$	a	70/0.1	42%	7.15	13	1730, 1654	258.0/4.43
$R^1 = (CH_2)_2CH_3$ $R^2 = (CH_2)_2CH=CH_2$	a[4])	120/0.2	60%	6.90	14	1675, 1637	267.5/4.35
$R^1 = CH_2C_6H_5$ $R^2 = (CH_2)_2CH=CH_2$	a	–	0%[5])	–	–	–	–
$R^1 = C_6H_5$ $R^2 = OCH_3$	a	110°/0.1 m.p. 56–57°	51%	not visible		1726, 1648	253.5/4.51

[3]) *Procedure a*: A mixture of 0.66 mol primary amine + 0.6 mol crotonaldehyde + 300 ml dry benzene + 140 g molecular sieve was stirred for 6 to 16 h at 25° [4], then filtered and evaporated to give crude **2** as an oily residue. To 0.012 mol of crude **2** in 15 to 60 ml of toluene at −40° with vigorous stirring under N_2 was added 8 ml of a 1.67 molar solution of sodium methylsulfinylmethide in DMSO [5]. After 0.5 h at −40° 0.015 mol of acyl chloride was added all at once, the mixture slowly warmed up to 0° within 3 h, kept at room temperature for another 2 h and finally washed several times with water. Evaporation of the dried solution and purification by chromatography (SiO_2) and/or distillation furnished the dienamides **4**.

Procedure b: as procedure a; however, instead of the sodium methylsulfinylmethide in DMSO 9 ml of a 2 molar solution of sodium hexamethyldisilazane in toluene was added to 0.012 mol of crude **2** in 15 ml of toluene at −40°.

[4]) The intermediate N-propyl-1-imino-2-butene was purified by distillation (b.p. 69–70°/68 Torr), prior to treatment with sodium methylsulfinylmethide at −60° followed by addition of allyl acetyl chloride at −60°.

[5]) This negative result may be attributed to predominant abstraction of a benzylic proton in **2** ($R^1 = CH_2C_6H_5$) by the base.

was required. Direct acylation of N-alkyl-1-imino-2-butenes **2**, readily prepared from crotonaldehyde **1** and primary amines, with carboxylic acid anhydrides in the presence of triethylamine or sodium acetate[2]) failed to give the desired dienamides **4**.

However, treatment of the conjugated azomethines **2** with strong bases, such as sodium methylsulfinylmethide or sodium hexamethyldisilazane at $-40°$ to $-60°$ in toluene, followed by the addition of a 1,25 equivalent of acyl chloride furnished stereoselectively the *trans*-N-acyl-1-amino-butadienes **4** (*Scheme*) in good yields. Typical spectral data and product yields are shown in Table 1.

The reaction sequence **2** → **4** presumably involves prior abstraction of a proton H_x by the base to give a delocalized anion **3**, which subsequently is acylated regioselectively at the nitrogen atom. The observed stereoselectivity accords with the W-conformation[6]) of the intermediate anion **3**.

In contrast to the relatively unstable N,N-diethyl-1-amino-1,3-butadiene [7] the dienamides **4** described here did not decompose on chromatography, distillation and storage over several months in the freezer. However they may undergo elimination to give **5** at temperatures greater than 200°. Thus, the diene **4** (R^1 = cyclohexyl, $R^2 = OCH_3$) at 215°/18 h in toluene (5% solution) was converted to the urethane **5** (R^1 = cyclohexyl, $R^2 = OCH_3$) [8] (50% yield).

The class of compounds exemplified by **4** presumably could serve as valuable diene component for both inter- and intra-molecular *Diels-Alder*-additions [1] [9].

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[2]) Under these conditions azomethines are converted effectively to N-acyl-enamines [3].
[6]) For evidence concerning the W-shape of the pentadienyl carbanion see [6].