ACID DIMERIZATION OF N-VINYL-4,5,6,7-TETRAHYDROINDOLE

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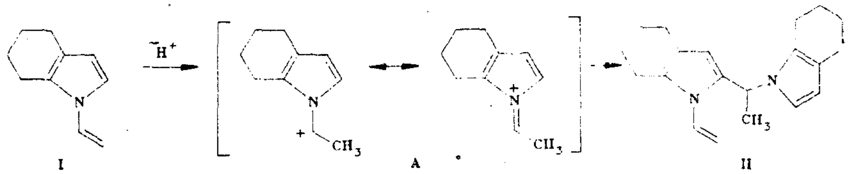
Reaction of N-vinyl-4,5,6,7-tetrahydroindole with acids, the chlorides of iron, tin or titanium, or with organochlorosilanes leads to formation of 1-vinyl-2-[1-(4,5,6,7-tetrahydroindol-1-yl)ethyl]-4,5,6,7-tetrahydroindole.

There are literature reports [1-3] of the reactions of N-vinylindoles and N-vinylpyrroles with halogens, hydrogen halides, organochlorosilanes, organochlorostannanes, and other compounds of acidic character. The basic course of such reactions is the formation of charge transfer complexes and polymerization at the N-vinyl double bond.

A study of the reaction of N-vinyl-4,5,6,7-tetrahydroindole (I) with catalytic amounts of HCl has shown a major, alternative reaction course resulting in electrophilic substitution of pyrrole hydrogen in one molecule by an immonium cation of a second molecule [4].

Continuing investigation of this reaction we have studied the behavior of I with a series of Brönsted and Lewis acids and have shown that, in each case, attack of immonium cation (A) on the pyrrole ring of I is certainly one (and sometimes the principal) reaction process.



I A II

IR, UV, ^{1}H NMR, ^{13}C NMR and mass spectrometric data for II were in agreement with [4-6].

The Brönsted and Lewis acid catalysts used included mineral and organic acids, the chlorides of iron, tin, and titanium, and alkylchlorosilanes (Table 1).

TABLE 1. Dimerization of N-Vinyl-4,5,6,7-tetrahydroindole in the Presence of Brönsted and Lewis Acids

Catalyst	Amount of catalyst, %	Reaction time, h	T, °C	Dimer yield, %
HCl	2	48	20	20
H_2SO_4	2	50	20	17
H_2SO_4	2	500	20	56
HNO_3	1	50	Effervescence on heating	11
MeCOOH	1	50	20	Traces
$FeCl_3$	2	50	20	Traces
$FeCl_3$	2	60	60	Traces
$TiCl_4$	2	50	20	Traces
$SnCl_4$	4	50	20	3
BF_3OEt_2	1	60	20	Traces
BF_3OEt_2	1	60	60	Traces
Et_3SiCl*	2	20	20	25
Et_3SiCl	2	20	20	68
Me_2SiCl_2	2	20	20	65
$Me_2EtSiCl$	2	20	20	32
Et_2SiCl_2	2	20	20	37
$PhMeSiCl_2$	2	20	20	18
$SiCl_4$	2	20	20	13

*Reaction under argon.

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The experimental results show that the most active dimerization catalysts were the organochlorosilanes with dimer yields reaching 68%.

Carrying out the reaction in the absence of air (using argon) led to a much lower dimer yield suggesting that the actual dimerization catalyst is hydrogen chloride liberated from the chlorosilane in the presence of atmospheric moisture.

The low activity of the metal chlorides ($FeCl_3$, $SnCl_4$, $TiCl_4$) may be due to their insolubility in I (the crystalline growth occurring only on the catalyst surface).

EXPERIMENTAL

N-Vinyl-2-[1-(4,5,6,7-tetrahydroindol-1-yl)ethyl]-4,5,6,7-tetrahydroindole (II). Dimethyldichlorosilane (0.03 g, 0.23 mmole) was added to the indole (I) (3.0 g, 20 mmole). After 20 h the reaction mixture was dissolved in hot hexane and filtered to remove insoluble material. Cooling of the hexane then gave transparent, pink crystalline dimer II (1.95 g, 65%) with mp 114°C.

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SYNTHESIS OF 8-PHENYL-10H-PYRIDO[1,2-*a*]INDOLE SALTS FROM 2,3,3-TRIMETHYL-3H-INDOLE CHLORIDES WITH CINNAMALDEHYDE

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Reaction of 2,3,3-trimethyl-3H-indole chloride with cinnamic and 4-dimethylaminocinnamic aldehydes led to salts of 8-phenyl and 8-(4-dimethylaminophenyl)-10,10-dimethyl-10H-pyrido[1,2-*a*]indole.

We have previously reported the synthesis of pyrido[1,2-*a*]indoles by the reaction of 3H-indole salts with α,β-unsaturated ketones [1-3]. Treatment of 2,3,3-trimethyl-3H-indole perchlorate with methylvinyl ketone in acetonitrile or without solvent [3-5] led to 1-(3-oxobutyl)-2,3,3-trimethyl-3H-indole perchlorate which cyclized on heating in pyridine to 8,10,10-trimethyl-10H-pyrido[1,2-*a*]indole perchlorate [3]. In contrast, the end product from reacting 2,3,3-trimethyl-3H-indole bromide with the same ketone in dimethylacetamide was 6,10,10-trimethyl-10H-pyrido[1,2-*a*]indole bromide. Aromatic α,β-unsaturated ketones [2, 3, 6] reacted with 3H-indole salts similarly. Phenyl-10H-pyrido[1,2-*a*]indole salts have found use as optical bleachers [2] and as dyes [7] for synthetic fibers.

We have found that annelation of the pyridine ring to 3H-indole occurs when 3H-indole chlorides Ia,b reacted with α,β-unsaturated aldehydes. Thus heating Ia with 4-dimethylaminocinnamaldehyde in acetonitrile gave IIa. 2,3,3-Trimethyl-3H-indole and its salts readily con-

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