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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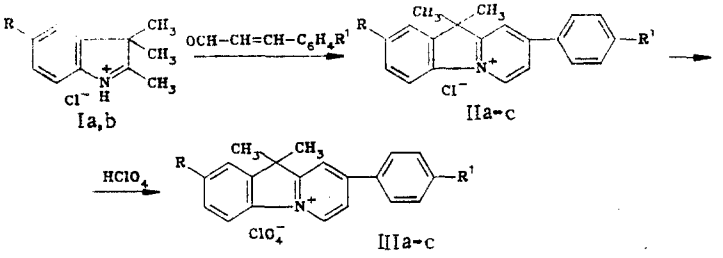
densed with different benzaldehydes to give 2-styrylindoles [8-11]. The formation of IIa salts with an aromatic substituent in the 8 position infers that the nitrogen atom of the indole ring (and not the 2-methyl group carbon) adds to the carbonyl carbon atom. The phenyl location in IIa was determined from the spin-spin coupling parameters for the pyridine ring protons in the PMR spectrum (J ortho, 6H-7H = 6.9; J meta, 7H-9H = 1.9 Hz) and the characteristic signal multiplicity [12].



I—III a R=H, b R=CH_3; II, III a,b R'=$N(CH_3)_2$, c R=R'=H

2,10,10-Trimehtylpyrido[1,2-α]indole (IIb) chloride was synthesized from Ib in the same way as IIa. Workup of IIa,b with perchloric acid gave the perchlorates IIIa,b. In contrast to the starting materials, these were soluble in chlorinated hydrocarbons and aprotic polar solvents. Chloride IIc could not be isolated pure from the reaction of salt Ia with cinnamaldehyde but when perchloric acid was added to this reaction mixture the perchlorate IIIc crystallized out.

EXPERIMENTAL

PMR spectra were recorded on a Tesla BS-487C (80 MHz) instrument (internal standard HMDS) and IR spectra on a UR-20 spectrometer (KBr pellets).

10,10-Dimethyl-8-(4-dimethylaminophenyl)-10H-pyrido[1,2-α]indole Chloride (IIa). A solution of Ia (1.96 g, 10 mmole) and 4-dimethylaminocinnamaldehyde (1.75 g, 10 mmole) in acetonitrile (15 ml) was heated for 3 h at 75°C. The mixture was cooled to 0°C and held at that temperature for 24 h. The precipitate was filtered off and recrystallized from 2-propanol to give 1.45 g (41%) with mp 290-291°C. IR Spectrum (cm^{-1}): 1650 (C=N), 1595 (C=C), 1475, 1450, 1378 (CH_3). PMR Spectrum (CD_3OD): 1.78 (6H, s, 10,10-CH_3), 3.09 (6H, s, N,N-CH_3), 6.73-8.13 8H, m, Ar excluding H-6,7,9), 8.19 (1H, dd, J_{7H-9H} = 1.9, J_{6H-7H} = 6.9 Hz, 7-H), 8.47 (1H, J = 1.9 Hz, 9-H), 9.21 ppm (1H, d, J = 6.9 Hz, 6-H). Found, %: Cl 9.9. $C_{22}H_{23}ClN_2$. Calculated, %: Cl 10.1.

10,10-Dimethyl-8-(4-dimethylaminophenyl)-10H-pyrido[1,2-α]indole Perchlorate (IIIa). A solution of 60% $HClO_4$ (0.67 g, 4 mmole) in water (5 ml) was added to IIa (1.05 g, 3 mmole) in a mixture of 2-propanol (2 ml) and water (5 ml). Filtration of the precipitate, washing with water and drying gave 1.0 g (80%) of the perchlorate IIIa which was recrystallized from acetonitrile to give 0.65 g (52%) with mp 282-283°C. IR Spectrum (cm^{-1}): 1648 (C=N), 1595 (C=C), 1477, 1440, 1375 (CH_3), 1098, 645 (ClO_4^-). PMR Spectrum (CD_3CN): 1.69 (6H, s, 10,10-CH_3), 3.09 (6H, s, N,N-CH_3), 6.84-8.08 (8H, m, Ar excluding H-6,7,9), 8.13 (1H, dd, J_{7H-9H} = 1.9, J_{6H-7H} = 6.9 Hz, 7-H), 8.29 (1H, d, J = 1.9 Hz, 9-H) 8.96 ppm (1H, J = 6.9 Hz, 6-H). Found, %: C 63.7, H 5.6, Cl 8.4. $C_{22}H_{23}ClN_2O_4$. Calculated, %: C 63.7, H 5.6, Cl 8.5.

8-(4-Dimethylaminophenyl-2,10,10-trimethyl-10H-pyrido[1,2-α]indole Chloride (IIb). This was obtained similarly to IIa from Ib (2.10 g, 10 mmole) and 4-dimethylaminocinnamaldehyde (1.75 g, 10 mmole) in 1.40 g (38%) yield with mp 199-200°C (from 2-propanol). PMR Spectrum (CD_3OD): 1.73 (6H, s, 10,10-CH_3), 2.52 (3H, s, 2-CH_3), 3.07 (6H, s, N,N-CH_3), 6.68-8.11 (7H, m, Ar excluding H-6,7,9), 8.13 (1H, dd, J_{7H-9H} = 1.9, J_{6H-7H} = 6.9 Hz, 7-H), 8.41 (1H, d, J = 1.9 Hz, 9-H), 9.13 ppm (1H, d, J = 6.9 Hz, 6-H). Found, %: Cl 9.6. $C_{23}H_{25}ClN_2$. Calculated, %: Cl 9.7.

8-(4-Dimethylaminophenyl)-2,10,10-trimethyl-10H-pyrido[1,2-α]indole Perchlorate (IIIb). This was obtained from chloride IIb (1.09 g, 3 mmole) and 60% $HClO_4$ (0.67 g, 4 mmole) similarly to IIIa in 0.9 g (70%) yield with mp 289-290°C (acetonitrile). IR Spectrum (cm^{-1}): 1648 (C=N), 1600 (C=C), 1480, 1450, 1378, 1325 (CH_3), 1098, 645 (ClO_4^-). PMR Spectrum: (CD_3CN): 1.72 (6H, s, 10,10-CH_3), 2.50 (3H, s, 2-CH_3), 3.11 (6H, s, N,N-CH_3), 6.76-8.03 (7H, m, Ar ex-

cluding H-6,7,9), 8.07 (1H, dd, J_{7H-9H} = 1.9, J_{6H-7H} = 6.9 Hz, 7-H), 8.26 (1H, d, J = 1.9, 9-H), 8.88 ppm (1H, d, J = 6.9 Hz, 6-H). Found, %: Cl 8.0. $C_{23}H_{25}ClN_2O_4$. Calculated, %: Cl 8.3.

10,10-Dimethyl-8-phenyl-10H-pyrido[1,2-α]indole Perchlorate (IIIc). A solution of Ia (5.87 g, 30 mmole) and cinnamaldehyde (3.96 g, 30 mmole) in acetonitrile (15 ml) was heated for 3 h at 75°C, cooled to 20°C, and alcohol (8 ml) followed by 60% $HClO_4$ (3.33 g, 20 mmole) were added. The mixture was kept at 0°C for 48 h, the crystalline product filtered off, and recrystallized from acetonitrile to give 1.5 g (13%) with mp 222-223°C. PMR Spectrum (CD_3CN): 1.79 (6H, s, 10,10-CH_3), 7.56-8.26 (9H, m, Ar excluding H-6,7,9), 8.34 (1H, dd, J_{7H-9H} = 1.9, J_{6H-7H} = 6.8 Hz, 7-H), 8.56 (1H, d, J = 1.9 Hz, 9-H), 9.31 ppm (1H, d, J = 6.8 Hz, 6-H). Found, %: C 64.5, H 4.8, Cl 9.5. $C_{20}H_{18}ClNO_4$. Calculated, %: C 64.6, H 4.9, Cl 9.5.

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CONVERSION OF 5-HYDROXY TO 5-AMINO AND 5-ALKOXYPYRAZOLIDINES

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1-Acyl-5-hydroxypyrazolidines readily exchange their hydroxyl group when treated with primary amines or alcohols to form the corresponding 5-amino or 5-alkoxypyrazolidines. An acid catalyst is needed for the preparaton of the 5-alkoxypyrazolidines.

We have previously shown that 1-acyl-5-hydroxypyrazolidines (obtained by condensation of alkenals with β-alkyl(aryl)hydrazides [1] readily exchange their hydroxyl group in reactions with hydrazines or hydroxylamines to form compounds in the linear β-hydrazinohydrazone (oxime) or cyclic (pyrazolidine) forms [2]. This work concerns the reaction of 5-hydroxypyrazolidines with other nucleophiles (amines and alcohols).

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