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ADDITION OF THIOPHENOLS TO N-VINYLPYRROLES

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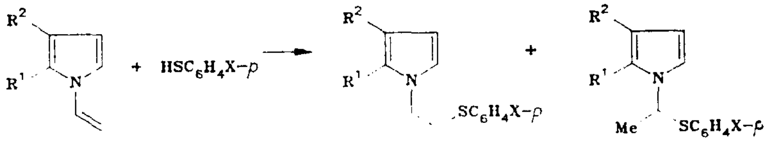
Thiophenols add to 1-vinyl-4,5,6,7-tetrahydroindole and 1-vinyl-2-phenylpyrrole in the presence of azobisisobutyronitrile to form 1-(2-arylthioethyl)pyrroles. The major products in the absence of initiator are the isomeric 1-(1-arylthioethyl)pyrrole α-adducts. NH-Pyrroles inhibit the radical process and form selectively the α-adducts.

N-Vinylpyrroles have become available via a new and effective method from ketoximes and acetylene in the superbase system KOH–DMSO [1, 2] and readily add hydrosilanes [3, 4], alcohols [5, 6], phenols [7], and thiols [8]. Alkane thiones add to N-vinylpyrroles in the presence of azobisisobutyronitrile (AIBN) and in the absence of the initiator to form N-(β-alkylthioethyl)pyrroles in high yields. Thus, N-vinylpyrroles can act as precursors to a large family of previously unknown N-ethyl pyrroles with different heteroatoms in the ethyl radical which show promise in terms of potential biological activity.

This publication continues our systematic study of the reactivity of N-vinylpyrroles with respect to the addition of thiophenols. It has been found that thiophenols add to pyrroles I and II under conditions of free radical initiation to form the 1-(2-arylthioethyl)pyrrole β-adducts III-V selectively. Analogous conditions without initiator lead to a mixture of only 20% of the β-adduct but up to 80% of 1-(1-arylthioethyl)pyrrole α-adducts VI and VII.



I, II   III - V   VI, VII

I $R^1-R^2=(CH_2)_4$; II $R^1=Ph$, $R^2=H$; III $R^1-R^2=(CH_2)_4$, $X=H$; IV $R^1-R^2=(CH_2)_4$, $X=F$; V $R^1=Ph$, $R^2=H$, $X=F$; VI $R^1-R^2=(CH_2)_4$, $X=H$; VII $R^1-R^2=(CH_2)_4$, $X=F$

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TABLE 1. Data for 1-(2-Arylthioethyl)- and 1-(1-Arylthioethyl)pyrroles

Compound	Empirical formula	bp, °C (mm Hg)	n_D^{20}	d_4^{20}	PMR spectrum, δ, ppm									Yield, %
					Ar	2-H	3-H	cyclohexyl		CH_2N	CH_2S	CH	CH_3	
								4,7-CH_2	5,6-CH_2					
III	$C_{16}H_{19}NS$	174 ... 176 (1)	1,5970	1,0961	7,00 ... 7,50	6,30	5,81	2,35	1,63	3,72 t	2,91 t	—	—	84
IV	$C_{16}H_{18}FNS$	198 ... 200 (2)	1,5840	1,1571	6,5 ... 7,3	6,31	5,85	2,34	1,63	3,74 t	2,90 t	—	—	86
V	$C_{18}H_{16}FNS$	175 ... 177 (1)	1,6103	1,1533	Ph 7,28, 7,11, 6,86	6,95 t	6,7 m	—	—	4,06	2,91	—	—	81
VI	$C_{16}H_{19}NS$	143 ... 145 (1,5)	1,5868	1,0752	7,00 ... 7,30	6,64	5,83	2,41	1,60	—	—	5,20	1,75	88
VII	$C_{16}H_{18}FNS$	160 ... 162 (2)	1,5750	1,1069	6,85 ... 7,20	6,64	5,85	2,39	1,57	—	—	5,17	1,72	90

Thiylation of a mixture of 1-vinyl-4,5,6,7-tetrahydroindole (28.5%), 4,5,6,7-tetrahydroindole (61%), and cyclohexanone oxime (10.5%), obtained according to [9], both with and without the AIBN initiator leads only to α-addition (VI, VII) while an NH-pyrrole inhibits the radical process and hinders β-adduct formation.

4-Nitrothiophenol does not add to indole I. Stirring this reaction mixture at room temperature causes a powerful exotherm and forms a polymer, probably similar to the oligomer formed in the presence of acid [10].

Hence, in contrast to alkane thiols which add to N-vinylpyrroles practically exclusively via a radical mechanism to form the β-adducts [8], the thiophenols show a marked tendency to electrophilic addition (on account of their increased acidity) and produce α-adducts (Table 1).

The PMR spectra of pyrroles III-V show the absence of $SCHCH_3$ protons and are in full agreement with their structures as 1-(2-arylthioethyl)pyrroles (Table 1). Similarly, the PMR spectra of pyrroles VI and VII shows the absence of SCH_2CH_2 signals and correspond to 1-(1-arylthioethyl)pyrroles.

EXPERIMENTAL

PMR spectra were recorded on a BS-567A (100 MHz) instrument with HMDS internal standard. Elemental analytical data (C, H, N, and F) for III-VII agreed with that calculated.

The starting N-vinylpyrroles were synthesized by a Trofimov reaction [1, 2].

1-(2-Phenylthioethyl)-4,5,6,7-tetrahydroindole (III). A mixture of indole I (2.94 g, 0.02 mole) and thiophenol (2.8 g, 0.025 mole) was heated for 20 h at 75°C in a sealed ampul in the presence of AIBN (0.03 g). Distillation in vacuo over finely powdered KOH gave III (4.3 g).

1-[2-(4-Fluorophenylthio)ethyl]-4,5,6,7-tetrahydroindole (IV) and 1-[2-(4-fluorophenylthio)ethyl]-2-phenylpyrrole (V) were obtained similarly.

1-(2-Phenylthioethyl)-4,5,6,7-tetrahydroindole (III) and (1-(1-Phenylthioethyl)-4,5,6,7-tetrahydroindole (VI). Pyrrole I (1.47 g, 0.01 mole) and thiophenol (1.1 g, 0.01 mole) were heated for 20 h at 75°C without initiator to give a mixture (1.52 g, 59%) containing indoles III (20%) and VI (80%) according to PMR spectroscopy.

1-[2-(4-Fluorophenylthio)ethyl]-4,5,6,7-tetrahydroindole (IV) and 1-[1-(4-Fluorophenylthio)ethyl]-4,5,6,7-tetrahydroindole (VII). Pyrrole I (1.47 g, 0.01 mole) and 4-fluorophenol (1.28 g, 0.01 mole) were heated for 20 h at 75°C. Distillation in vacuo over finely powdered KOH gave a mixture (1.68 g, 61%) which contained indoles IV (20%) and VII (80%).

1-(1-Phenylthioethyl)-4,5,6,7-tetrahydroindole (VI) was prepared similarly from a mixture (1.95 g) containing indole I (28.5 %), 4,5,6,7-tetrahydroindole (61%), and cyclohexanone oxime (10.5%) (prepared as in [9]) with thiophenol (0.6 g, 0.005 mole). Heating for 20 h at 75°C without initiator gave indole VI (0.86 g, 88%).

The same quantities of reagents and conditions in the presence of AIBN (0.03 g) gave indole VI (0.85 g, 87%).

1-[1-(4-Fluorophenylthio)ethyl]-4,5,6,7-tetrahydroindole (VII). Heating a mixture (1.47 g) of indole I (28.5%), 4,5,6,7-tetrahydroindole (61%), cyclohexanone oxime (10.5%), and 4-fluorothiophenol (1.28 g, 0.01 mole) for 20 h at 75°C without initiator gave indole VII (0.7 g, 90%).

With the same quantities and conditions but using AIBN (0.03 g), indole VII (0.68 g, 87%) was obtained.

Reaction of 1-Vinyl-4,5,6,7-tetrahydroindole (I) with 4-Nitrothiophenol. Stirring a mixture of indole I (1.47 g, 0.01 mole), 4-nitrothiophenol (1.55 g, 0.01 mole), and AIBN (0.03 g) caused a powerful exotherm and formation of a polymer which was not investigated in detail. A similar result was obtained without the initiator.

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FIVE-MEMBERED 2,3-DIOXOHETEROCYCLES

15.* SYNTHESIS AND [1,3]-SIGMATROPIC REARRANGEMENT OF 1,5-DIARYL-3-DIPHENYLMETHOXY-4-ETHOXYCARBONYL-2,5-DIHYDROPYRROL-2-ONES

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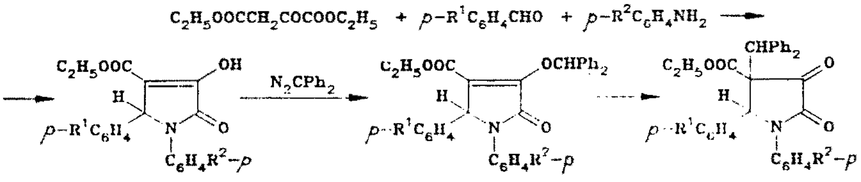
Ethyl oxaloacetate reacts with a mixture of an aromatic aldehyde and an arylamine to give 1,5-diaryl-4-ethoxycarbonyltetrahydropyrrole-2,3-diones, which react with diphenyldiazomethane to give the O-alkylation products. On heating, the latter undergo suprafacial [1,3]-sigmatropic rearrangement to 1,5-diaryl-4-diphenylmethyl-4-ethoxycarbonyltetrahydropyrrole-2,3-diones. The effects of the type of migrating group on the rearrangement are discussed.

3-Diphenylmethoxy-substituted tetrahydrofuran- and tetrahydropyrrole-2,3-diones are convenient models for the study of [1,3]- and [1,5]-sigmatropic rearrangements in heterocyclic systems, in which the nature of the electron-acceptor group has a marked effect on the type of migration [2, 3].

In order to examine further the influence of the nature of the substituent in the 4-position of the heterocycle, we have obtained the 1,5-diaryl-4-ethoxycarbonyltetrahydropyrrole-2,3-diones (Ia, c-e) (Table 1), and examined their reactions with diphenyldiazomethane, and the thermal isomerization of the resulting O-alkyl derivatives (IIa-e).



Ia, c-e IIa-e IIIa-e

I-IIIa, e $R^1 = H$, b $R^1 = Br$, c $R^1 = CH_3O$, d $R^1 = NO_2$, a-d $R^2 = H$, e $R^2 = NO_2$

The IR spectra of (Ia, c-e) (Table 2) show absorption for the ester carbonyl at 1700-1721 cm^{-1}, lactam carbonyl at 1670-1687 cm^{-1}, the double bond at 1610-1655 cm^{-1}, and for the enol hydroxy at 3270-3310 cm^{-1}. In the PMR spectra, in addition to a multiplet for the aromatic protons at 6.98-7.55 ppm and signals for the ethoxy group, signals were observed for

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*For Communication 14, see [1].

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