PYRROLES FROM KETOXIMES AND ACETYLENE.

28.* INVESTIGATION OF VINYL CHLORIDE INSTEAD OF ACETYLENE FOR THE SYNTHESIS OF ARYLPYRROLES FROM ARYLETHANONE OXIMES

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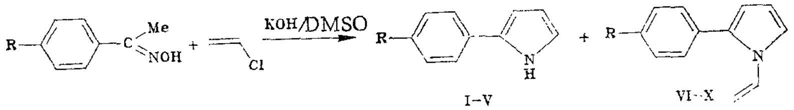
2-Arylpyrroles and their N-vinyl derivatives have been synthesized by reacting arylethanone oximes with vinyl chloride in a KOH—DMSO system at 140°C.

We recently showed [4] in the example of oximes of aliphatic ketones [2, 3] and α-tetralone that vinyl chloride can be an acceptable substitute for free acetylene in the synthesis of pyrroles and N-vinylpyrroles according to the Trofimov reaction. In this communication we shall present data on the reaction of vinyl chloride with arylethanone oximes, and we shall give the first detailed description of the experimental conditions for carrying out such a reaction. In a KOH—DMSO system these ketoximes react with vinyl chloride to form the corresponding 2-arylpyrroles (I-V) and their N-vinyl derivatives (VI-X):



I, VI R=H; II, VII R=Me; III, VIII R=Et; IV, IX R=*i*-Pr; V, X R=*t*-Bu

The reaction is effective only when a five- to sixfold molar excess of potassium hydroxide is used.

EXPERIMENTAL

The PMR spectra of 10% solutions of the compounds were measured on a Varian T-60 spectrometer in CCl_4 with HMDS as an internal reference. The IR spectra were recorded on a Shimadzu UR-430 spectrometer (Japan) in the 2000-330-cm^{-1} region in liquid petrolatum and in the 5000-2000-cm^{-1} region in hexachlorobutadiene.

2-Phenylpyrrole (I) and 1-Vinyl-2-phenylpyrrole (VI). A 31.2-g portion (0.5 mole) of vinyl chloride is bubbled over the course of 2 h 30 min through a suspension of 150 ml of DMSO, 33.6 g (0.6 mole) of KOH, and 13.5 g (0.1 mole) of acetophenone oxime heated to 140°C with thorough stirring. After this the stirring and heating are continued for an additional 30 min. The reaction mixture is cooled to room temperature, diluted with cold water, and extracted five times with benzene. The extract is washed three times with a 30% KOH solution and dried with potassium carbonate, the benzene is driven off, and the residue is vacuum-distilled. This gives a mixture of pyrrole I and 1-vinylpyrrole VI, from which the bulk of the pyrrole is recovered by crystallization from isooctane. The portion of pyrrole I remaining in the mother solution and 1-vinylpyrrole VI are separated chromatographically in a thin layer of silica gel (LS5/40 μ) in a 1:2 ether—hexane system. The individuality of compounds I and VI are additionally confirmed by TLC on Silufol. This gives 6.4 g (45%) of pyrrole I, mp 129°C. According to the data in [5], the mp is 129°C. PMR spectrum: 7.97 (NH);

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*For report 27 see [1].

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6.4, 6.1, 5.9 (protons of the pyrrole ring); 7.0 ppm (Ph). IR spectrum: 3410, 3365 (NH); 1686 (deform. NH); 700, 1377, 1500 (pyrrole ring); 1500, 1600 (benzene ring); 762 cm^{-1} (deform. C—H of monosubstituted benzene ring).

At the same time, 1.2 g (7%) of 1-vinylpyrrole VI with bp 102°C (2.67 hPa), n_D^{20} 1.6194, d_4^{20} 1.0438 are isolated. According to the data in [6]: bp 94°C (1.33 hPa), n_D^{20} 1.6190, d_4^{20} 1.0443.

2-(p-Tolyl)pyrrole (II) and 1-Vinyl-2-(p-tolyl)pyrrole (VII). According the the method just described, 3.1 g (39%) of pyrrole II with mp 150°C is obtained from 7.45 g (0.05 mole) of 1-(p-toyl)ethanone oxime (mp 85°C), and 15.6 g (0.25 mole) of vinyl chloride in the presence of 16.8 g (0.3 mole) of KOH and 150 ml of DMSO (3 h, 140°C). According to the data in [7], the mp is 153-154°C. In addition, 1.2 g (13%) of 1-vinylpyrrole VII with bp 124°C (2.67 hPa), n_D^{20} 1.6081, and d_4^{20} 1.0245 are isolated. According to the data in [8]: bp 104°C (2.67 hPa), n_D^{20} 1.6070, d_4^{20} 1.0250. PMR spectrum of pyrrole II: 7.77 (NH); 6.33, 6.05, 5.83 (protons of the pyrrole ring); 7.0, 6.87, 6.78, 6.67 H of the benzene ring); 2.28 ppm (CH_3). IR spectrum of pyrrole II: 3364 (NH); 1652 (deform. NH); 736, 1382, 1514 (pyrrole ring); 1382, 1464 (benzene ring); 805 (deform. C—H, 1,4-disubstituted benzene); 2812, 2887, 2955, 3023 cm^{-1} ($H—C_{sp^3}$).

2-(p-Ethylphenyl)pyrrole (III) and 1-Vinyl-2-(p-ethylphenyl)pyrrole (VIII). A 3.5-g (41%) portion of pyrrole III with mp 140-142°C is obtained from 8.15 g (0.05 mole) of vinyl chloride in the presence of 16.8 g (0.3 mole) of KOH and 150 ml DMSO (3 h, 140°C). According to the data in [8], the mp is 148-149°C. At the same time, 1.1 g (11%) of 1-vinylpyrrole VIII with bp 123°C (1.33 hPa), n_D^{20} 1.5952, and d_4^{20} 1.0169 are recovered. According to the data in [9](bp 126-127°C (1.33 hPa), n_D^{20} 1.5979, and d_4^{20} 1.0175. PMR spectrum of pyrrole III: 7.62 (NH); 6.23, 6.06, 5.87 (protons of the pyrrole ring); 6.95, 6.82, 6.75, 6.83 (q, protons of the benzene ring); 2.72, 2.6, 2.5, 2.37, center at 2.55 (q, CH_2); 1.33, 1.2, 1.07 ppm (m, CH_3). IR spectrum of pyrrole III: 3409 (NH), 1655 (deform. NH), 714, 1377, 1511 (pyrrole ring); 1455, 1575 (benzene ring); 836 (deform. =C—H 1,4-disubstituted benzene); 2909, 2954 cm^{-1} ($H—C_{sp^3}$).

2-(p-Isopropylphenyl)pyrrole (IV) and 1-Vinyl-2-(p-isopropylphenyl)-pyrrole (IX). An 8-g portion (43%) of pyrrole IV with mp 108°C is obtained from 17.7 g (0.1 mole) of 1-(4-isopropylphenyl)ethanone oxime (mp 55-56°C) and 31.3 g (0.5 mole) of vinyl chloride in the presence of 33.6 g (0.6 mole) of KOH and 150 ml of DMSO (3 h, 140°C). Found: C, 84.8; H, 7.9; N, 7.4%. Calculated for $C_{13}H_{15}N$: C, 84.3; H, 8.2; N, 7.6%. PMR spectrum of pyrrole IV: 7.7 (NH); 6.26, 6.04, 5.87 (protons of the pyrrole ring); 7.00, 6.85, 6.77, 6.67 (q, protons of the benzene ring); 2.85, 2.73, 2.65, 2.53 (q, CH_2); 1.27, 1.13 ppm (d, CH_3). IR spectrum of pyrrole IV: 3375 (NH); 1645 (deform. NH); 714, 1373, 1503 (pyrrole ring); 1448 (benzene ring); 832 (deform. =C—H 1,4-disubstituted benzene); 2841, 2887, 2932 cm^{-1} ($H—C_{sp^3}$). At the same time, 2.4 g (11%) of 1-vinylpyrrole IX with bp 140°C (2.67 hPa), n_D^{20} 1.5743, and d_4^{20} 0.9891 are recovered. Found: C, 85.7; H, 8.5%. Calculated for $C_{15}H_{17}N$: C, 85.3; H, 8.1%.

2-(p-tert-Butylphenyl)pyrrole (V) and 1-Vinyl-2-(p-tert-butylphenyl)-pyrrole (X). A 4.1-g portion (41%) of pyrrole V with mp 109-110°C is obtained from 9.55 g (0.05 mole) of 1-(4-tert-butyphenyl)ethanone oxime and 15.6 g (0.25 mole) of vinyl chloride in the presence of 16.8 g (0.3 mole) of KOH and 150 ml of DMSO (3 h, 140°C). Found: C, 84.8; H, 8.2; N, 7.0%. Calculated for $C_{14}H_{17}N$: C, 84.41 H, 8.6; N, 7.0%. PMR spectrum of pyrrole V: 7.65 (NH); 6.18, 6.07, 5.87 (protons of the pyrrole ring); 6.83 (s, protons of the benzene ring); 1.23 ppm (s, CH_3). IR spectrum of pyrrole V: 3432 (NH); 1661 (deform. NH); 734, 1366, 1477 (pyrrole ring); 1457 (benzene ring); 845 cm^{-1} (deform. =C—H 1,4-disubstituted benzene). At the same time, 1.6 g (14%) of 1-vinylpyrrole of X with bp 131°C (2.67 hPa), n_D^{20} 1.5796, and d_4^{20} 0.9876 are recovered. Found: C, 84.8; H, 8.4%. Calculated for $C_{16}H_{19}N$: C, 85.3; H, 8.5%.

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CONVERSIONS OF 1-ARYLAMINO-3-PHENYLOXINDOLES

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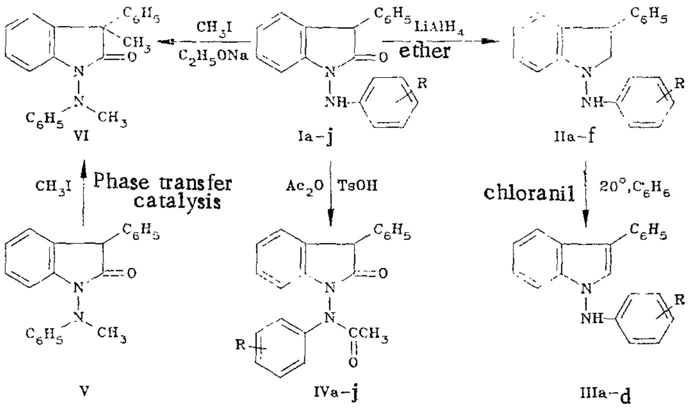
Acetylation of 1-arylamino-3-phenyloxindoles by acetic anhydride in the presence of an acidic catalyst (TsOH) gives N-acetyl derivatives; alkylation by methyl iodide in the presence of sodium ethoxide gives $C_{(3)}$- and N-dimethyl derivatives. Reduction by lithium aluminum hydride gives 1-arylamino-3-phenylindolines, which form the corresponding indoles when they are oxidized by chloranil.

The synthesis of 1-arylamino-3-phenyloxindoles was previously described in [1]. In this communication we shall consider some reactions of these compounds. The general scheme of the conversions studied is as follows:



The reduction of compounds Ia–f by lithium aluminum hydride in ether takes place with preservation of the N—N bond [2]. The reaction products are the corresponding indolines IIa–f, and their characteristics are given in Table 1. They are colorless crystalline substances, which are highly soluble in organic solvents. Owing to the presence of two enantiomeric forms of compounds IIa–f at the $C_{(3)}$ ring atom, the signal of the protons of the CH_2 group in the PMR spectra (CCl_4) is displayed in the form of two triplets at 3.63–3.85 and 4.05–4.36 ppm, and the 3-H proton also produces a triplet at 2.82–3.09 ppm. The signals of the NH group are found at 4.63–4.83 ppm. Indolines IIa–f are stable with respect to oxidation in air, except for compound IIc, which is oxidized within 24 h in an ethanolic solution (monitoring accroding to the UV spectrum). Partial oxidation is clearly attributable to the formation of a small quantity of indole IIIc during the isolation of indoline IIc (see Experimental).

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