# PYRROLES FROM KETOXIMES AND ACETYLENE.

## III.* SYNTHESIS OF 2-ARYL- AND 1-VINYL-2-ARYLPYRROLES

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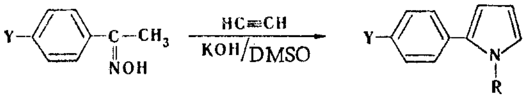
2-Aryl- and 1-vinyl-2-pyrroles were synthesized by condensation of p-substituted acetophenone oximes with acetylene under pressure in superalkaline media (KOH/DMSO). The initially formed nitrogen-unsubstituted pyrroles can be vinylated in the presence of acetylene. Lithium hydroxide, which is completely inactive in the vinylation step, was found to be a selective catalyst for the construction of a pyrrole ring from oximes of aliphatic aromatic ketones. In the case of aliphatic and cycloaliphatic ketoximes (for example, cyclohexanone oxime) LiOH has virtually no catalytic effect on the reaction. The yields of 1-vinyl-2-arylpyrroles depend substantially on the substituent in the phenyl ring. The structures of the synthesized compounds were confirmed by the IR, PMR, UV, and $^{13}C$ NMR spectra.

In an investigation of the possibility of a new pyrrole synthesis [2, 3] based on the reaction of ketoximes with acetylene we extended it to methyl aryl ketoximes and found that this method can be successfully used to obtain the previously unknown 1-vinyl-2-arylpyrroles (I-VI) and the difficult-to-obtain 2-arylpyrroles (VII, VIII).



I–VI R=CH=CH$_2$; VII, VIII R=H; I Y=H; II Y=C$_2$H$_5$; III Y=Cl; IV Y=Br;
V Y=CH$_3$O; VI Y=C$_6$H$_5$O; VII Y=H; VIII Y=C$_6$H$_5$O

The reaction proceeds smoothly at 100°C in the presence of 30% (based on the weight of the ketoxime) KOH in dimethyl sulfoxide (DMSO) in an autoclave at an initial acetylene pressure of 8-16 atm. The maximum pressure generated when the reaction mixture is warmed up to a given temperature is 20-25 atm; at this point pronounced acetylene absorption begins, and the pressure drops rapidly. At least a twofold excess of acetylene is used for the preparation of 1-vinlypyrroles (I-VI). As we have already noted [4], the initially formed nitrogen-unsubstituted pyrroles can be vinylated in the presence of acetylene. The ease of vinylation of pyrroles under the conditions of this reaction has been proved experimentally [5]. If it is necessary to obtain the corresponding NH pyrrole, the synthesis is carried out with the calculated amount of acetylene or with insufficient acetylene. Lithium hydroxide, which is completely inactive in the vinylation step, was found to be a selective catalyst for the construction of a pyrrole ring from oximes of aliphatic aromatic ketones. When this catalyst is used, strict proportioning of the amount of acetylene is not necessary. For example, this method was used to obtain 2-phenylpyrrole (VII) in 64% yield. It is interesting that LiOH has virtually no catalytic effect on the reaction in the case of aliphatic and cycloaliphatic ketoximes (for example, cyclohexanone oxime).

The yields and some of the physical constants of 1-vinyl-2-arylpyrroles (I-VI) are given in Table 1. It can be seen from Table 1 that the yields of 1-vinyl-2-arylpyrroles depend substantially on substituent Y. The sharp decrease in the yield of pyrrole IV (from p-bromoacetophenone oxime) is in comformity with principle: The low yield is due to saponification

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*See [1] for communication II.

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TABLE 1. Yields and Physicochemical Constants of 1-Vinyl-2-arylpyrroles

| Compound | Yield, % | bp, °C (mm) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|
| I | 71 | 94 (1) | 1,6200 | 1,0443 |
| II | 72 | 126—127 (1—0,5) | 1,5979 | 1,0175 |
| III | 65 | 120 (1—0,5) | 1,6290 | 1,1674 |
| IV | 22 | 123—124 (1—0,5) | 1,6469 | 1,3860 |
| V | 44 | 142—144 (1) | 1,6075 | 1,0857 |
| VI | 55 | 188—190 (1) | 1,6150 | 1,0953 |

of bromine by the strong base. When Y = $NO_2$, we were unable to obtain a pyrrole under the investigated conditions because of the instability of the substituent in the supralkaline medium (KOH/DMSO). The corresponding pyrrole was obtained in 43% yield from p-phenoxyacetophenone oxime and acetylene when the reaction temperature was lowered to 80°C.

The structures of the synthesized compounds were confirmed unambiguously by the IR, PMR, UV, and $^{13}C$ NMR spectra (the latter will be the subject of a special publication).

## EXPERIMENTAL

The IR spectra of films of 1-vinyl-2-arylpyrroles (I-VI) and KBr pellets of the 2-arylpyrroles (VII, VIII) were recorded with a UR-20 spectrometer. The PMR spectra of $CCl_4$ solutions of the compounds were obtained with a Tesla BS-4878 spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The UV spectra of cyclohexane solutions of the compounds were obtained with a Unicam spectrophotometer.

Acetophenone oxime was synthesized by the method in [6] (the p-ethyl-, p-chloro-, p-bromo-, p-methoxy, and p-phenoxyacetophenones were kindly furnished by Professor M. S. Shvartsberg, to whom the authors express their gratitude).

1-Vinyl-2-phenylpyrrole (I). A mixture of 6.75 g (0.05 mole) of acetophenone oxime (mp 56-58°C), 2.25 g of KOH, 50 ml of DMSO, and acetylene was heated under pressure (initial pressure 12 atm) in a 1-liter rotating autoclave at 100°C for 3 h, after which the mixture was diluted with a threefold (by volume) amount of water, and the aqueous mixture was extracted with ether. The extract was dried with $MgSO_4$, the ether was removed, and the residue was fractionated *in vacuo* to give 6 g of pyrrole I. IR spectrum: 586, 872, 976, 1588, and 1642 (vinyl group): 704 and 1360 (pyrrole ring): 1323 (C—N for N-substituted pyrroles); 1500 and 1602 cm$^{-1}$ (Ph). PMR spectrum: 4.98 (d, β-H$_{trans}$), 4.49 (d, β-H$_{cis}$), 6.79 (q, α-H), 6.10 (d, 3-H, 4-H), 6.95 (t, 5-H), and 7.2 ppm (m, Ph). UV spectrum, λ$_{max}$ (ε): 208 (12,900), 250 (12,700), and 270 nm (13,300). Found: C 85.1; H 6.6; N 8.1%. $C_{12}H_{11}N$. Calculated: C 85.4; H 6.6; N 8.3%. 1-Vinylpyrroles II-VI were similarly obtained (see Table 1 for the physical constants and yields).

1-Vinyl-2-(p-ethylphenyl)pyrrole (II). This compound was obtained from p-ethylacetophenone oxime (mp 82-83°C). IR spectrum: 1642 (vinyl group); 2870, 2930, and 2965 cm$^{-1}$ (H—C$_{sp^3}$). PMR spectrum: 5.04 (d, b-H$_{trans}$), 4.55 (d, β-H$_{cis}$), 6.85 (q, α-H), 6.02 (d, 3-H, 4-H), 7.03 (t, 5-H), 7.17 (m, Ph), 1.23 (t, $CH_3$), and 2.62 ppm (q, $CH_2$). UV spectrum, λ$_{max}$ (ε): 210 (11,700), 250 (12,800), and 265 nm (13,000). Found: C 85.8; H 7.6; N 7.0%. $C_{14}H_{15}N$. Calculated: C 85.2; H 7.7; N 7.1%.

1-Vinyl-2-(p-chlorophenyl)pyrrole (III). This compound was obtained from p-chloroacetophenone oxime (mp 86-87°C). IR spectrum: 592, 855, 968, and 1622 (vinyl group); 7.5, 1355, and 1540 (pyrrole skeleton); 1310 (C—N for N-substituted pyrroles); 1490 and 1562 (Ph); 795 cm$^{-1}$ (C—Cl). PMR spectrum: 5.07 (d, β-H$_{trans}$), 4.60 (d, β-H$_{cis}$), 6.48 (q, α-H), 5.76 (d, 3-H, 4-H), 6.84 (t, 5-H), and 7.02 ppm (m, Ph). UV spectrum, λ$_{max}$ (ε): 206 (14,600), 250 (11,400), and 270 (12,600). Found: C 70.9; H 4.9; N 6.8; Cl 17.7%. $C_{12}H_{10}ClN$. Calculated: C 70.8; H 4.9; N 6.9; Cl 17.4%.

1-Vinyl-2-(p-bromophenyl)pyrrole (IV). This compound was obtained from p-bromoacetophenone oxime (mp 127-128°C). IR spectrum: 598, 873, 965, and 1648 (vinyl group); 718, 1556, 1500, and 1575 (pyrrole ring, Ph); 1322 (C—N for N-substituted pyrroles); 500-600 cm$^{-1}$ (C—Br). PMR spectrum: 4.98 (d, β-H$_{trans}$), 4.42 (d, b-H$_{cis}$), 6.49 (q, α-H), 6.06 (d, 3-H, 4-H), 6.86 (t, 5-H), and 7.12 ppm (m, Ph). Found: C 58.9; H 4.1; Br 32.0; N 5.7%. $C_{12}H_{10}BrN$. Calculated: C 58.1; H 4.0; Br 32.2; N 5.7%.

1-Vinyl-2-(p-methoxyphenyl)pyrrole (V). This compound was obtained from p-methoxyacetophenone oxime (mp 86-87°C). IR spectrum: 592, 855, 968, and 1622 (vinyl group); 718, 1338, and 1540 (pyrrole skeleton); 1300 (C—N for N-substituted pyrroles); 1495, 1560, and 1597 (Ph); 1404 (C—O); 2845, 2940, and 2965 cm$^{-1}$ ($H{-}C_{sp^3}$). PMR spectrum: 5.01 (d, $\beta$-$H_{trans}$), 4.52 (d, $\beta$-$H_{cis}$), 6.75 (q, $\alpha$-H), 6.07 (d, 3-H, 4-H), 6.80 (t, 5-H), and 7.12 ppm (m, Ph). Found: C 78.9; H 6.9; N 7.0%. $C_{13}H_{13}NO$. Calculated: C 78.4; H 6.6; N 7.3%.

1-Vinyl-2-(p-phenoxyphenyl)pyrrole (IV). This compound was obtained from p-phenoxyacetophenone oxime. IR spectrum: 586, 968, and 1642 (vinyl group); 710, 1500, and 1592 (Ph); 1080 cm$^{-1}$ (C—O). PMR spectrum: 4.93 (d, $\beta$-$H_{trans}$), 4.27 (d, $\beta$-$H_{cis}$), 6.55 (q, $\alpha$-H), 6.00 (d, 3-H, 4-H), 6.89 (t, 5-H), and 7.07 ppm (m, Ph). Found: C 82.0; H 5.7; N 5.4%. $C_{18}H_{15}NO$. Calculated: C 82.7; H 5.8; N 5.4%.

2-Phenylpyrrole (VII). A mixture of 6.75 g (0.05 mole) of acetophenone oxime, 1.34 g of LiOH, 50 ml of DMSO, and acetylene was heated under pressure (initial pressure 12 atm) in a 1-liter rotating autoclave, after which the mixture was diluted with a threefold (by volume) amount of water, and the aqueous mixture was extracted with ether. The ether was removed from the extract, and the residue was subjected to steam distillation. The resulting 2-phenylpyrrole in the form of white plates with a mother-of-pearl luster were removed by filtration and dried between filter paper to give 4.6 g (64%) of VII with mp 129°C (in agreement with the literature data [7]). IR spectrum: 3400 and 3438 (NH); 698, 1500, and 1607 cm$^{-1}$ (Ph, pyrrole ring). PMR spectrum: 8.03 (MH); 6.65, 6.36, and 5.92 (pyrrole ring H, J = 3 Hz); 7.27 ppm (m, Ph).

2-(p-Phenoxyphenyl)pyrrole (VIII). This compound was obtained from the reaction of 11 g (0.048 mole) of p-phenoxyacetophenone oxime, 3.3 g of KOH, and 50 ml of DMSO, and acetylene after reaction at 80°C and an initial acetylene pressure of 14 atm for 4 h. The mixture was diluted with 300 ml of water, and the aqueous mixture was extracted with ether. The ether extracts were washed with water and dried with $MgSO_4$. Removal of the ether gave 9 g of a claret-brown crystalline substance. Recrystallization from 70% ethanol gave 4.8 g (43%) of pyrrole VIII with mp 152-154°C. IR spectrum: 3405 and 3445 (NH); 720, 1497, 1540, 1504, and 1596 cm$^{-1}$ (pyrrole ring and Ph). Found: C 81.6; H 5.4; N 5.6%. $C_{16}H_{13}NO$. Calculated: C 81.4; H 5.5; N 6.0%.

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