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NEW EXAMPLES OF THE VINYLATION OF NH-HETEROCYCLES WITH ACETYLENE AT ATMOSPHERIC PRESSURE IN THE KOH—DMSO SYSTEM

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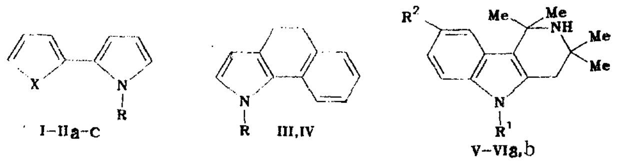
Vinylation of 2-hetarylpyrroles, 4,5-dihydrobenzo[g]indole, and 1,2,3,4-tetrahydro-γ-carbinols at atmospheric pressure in the superbasic system KOH—DMSO at 100-120°C has given the corresponding N-vinyl derivatives in yields of 92-99%.

Until recently, the N-vinylation of heterocycles with acetylene was carried out under a pressure of 20-40 atm at 160-200°C. In view of the explosive hazards of this reaction, its preparative use was extremely limited, and this has substantially retarded the development of the chemistry of N-vinylheterocycles.

It has recently been shown that the superbasic KOH—DMSO catalytic system enables the vinylation of alkyl- and arylpyrroles to be carried out at atmospheric pressure and temperatures as low as 100-120° (see [1] and the citations therein).

The object of this investigation was to assess to what extent this novel method was suitable for the synthesis of N-vinyl derivatives of other heterocycles.

The subjects chosen for study were the 2-hetarylpyrroles Ia, b, 4,5-dihydrobenzo[g]indole (III), and the 1,2,3,4-tetrahydro-γ-carbinols Va,b, 2-phenylpyrrole (Ic) being taken for comparison with the corresponding 2-furyl- (Ia) and 2-thienyl- (Ib) pyrroles.



I–IIa–c III,IV V–VIa,b

Ia–c, III R=H, IIa–c, IV R=CH=CH$_2$; I, II a X=O, b X=S, c X=CH=CH; Va,b R^1=H, VIa, b R^1=CH=CH$_2$; V, VI a R^2=H, b R^2=Me

The reaction was carried out in a glass flask with a stirrer. Acetylene was passed into the reaction mixture at atmospheric pressure. When vinylating the 2-hetarylpyrroles Ia,b and 2-phenylpyrrole Ic, a fivefold exceys of KOH was employed. The progress of the reaction was followed by GC. Chromatographically pure N-vinylpyrroles IIa,b were obtained by a single

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TABLE 1. Effect of Reaction Time and Temperature on the Yields and Proportions of N-Vinylpyrroles IIa-c

T_{react}, °C	Reaction time, h	Ratio (yield) of compounds,* %		
		Ia :IIa (yield of IIa)	Ib :IIb (yield of IIb)	Ic :IIc (yield of IIc)
110	3	28 : 72	49 : 51	50 : 50
110	4	2 : 98	15 : 85	
110	4,5	Trace ~100 (98)	3 : 97	12 : 78
110	5		Trace ~100 (98,5)	5 : 95
110	5,5			2 : 98
110	6			Trace ~100 (96)
120	1	23 : 57	38 : 62	24 : 76
120	2	10 : 90	25 : 75	15 : 85
120	3	Trace ~100 (86)	5 : 95	7 : 93
120	4		Trace ~100 (82)	Trace ~100 (87)

*Ratios were found by GC, and yields after distillation.

TABLE 2. Results of the Vinylation of Tetrahydro-γ-carbolines Va,b (sevenfold molar excess of KOH)

T, °C	Yield of N-vinyl derivative, %			
	P 720 mm Hg		P_{init} 10-12 atm P_{max} 20-30 atm	
	VIa	VIb	VIa	VIb
	Reaction time 6 h			
95	93,7			
100		97,5		
120	92,5	99,0		
	Reaction time 3 h			
100			90,4	
110				98,5
120			78,3	84,1

vacuum distillation of the crude product. Nearly quantitative yields (96-99%) were attained at 110°C after 4-5-6 h (Table 1). When the temperature was raised to 120°C, the time required for vinylation was reduced by 1.5-2 h, but the yields of N-vinylpyrroles decreased by 9-16% as a result of side reactions.

It is interesting that when an autoclave was used (initial pressure of acetylene 10-14 atm, maximum 20-30 atm, DMSO, threefold molar excess of KOH, 120°C), the yields of N-vinylpyrroles IIa-c were only 80% as a result of resinification and the difficulty of workup of the reaction mixture. Therefore, vinylation at atmospheric pressure is both safer and more efficient.

From the data presented in Table 1, the rate of vinylation of pyrroles increases in the sequence Ic < Ib < Ia, which is the same as the order of increasing NH-acidity [1],* and consequently, of decreasing nucleophilicity of their anions. Hence, this sequence of reactivity of the pyrroles Ia-c is not in accordance with the nucleophilic nature of the reaction, although it fully conforms withthe general behavior previously established by Skvortsova et al. [2], that the rate of base-catalyzed additions to acetylene of structurally related azoles increases as their acidity is increased. This contradiction is resolved when it is borne in mind that the reaction involves ion pairs, rather than the free anions. In such a case, the more 'acidic' azoles should form 'looser' ion pairs, and the introduction of acetylene at the ionic bond $> N...K^+$ is facilitated.

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*Trofimov and Mikhaleva [1] do not report a value for the acidity of 2-(2-furyl)pyrrole, but this can be calculated by the relationship they give between the pK_a value and the inductive constants of the substituents in the pyrrole ring.

The same type of behavior is shown in the vinylation of 4,5-dihydrobenzo[g]indole (III), which is less acidic than 2-phenylpyrrole (pK_a values 22.2 and 21.6 [1]), and therefore adds to acetylene less readily. In this case, in order to obtain the vinyl derivative IV in 97% yield, it is necessary to carry out the reaction at 120°C for 8 h, adding the alkali (threefold molar excess) to the reaction mixture portionwise in order to avoid resinification.

Comparison of the results of the vinylation of the tetrahydro-γ-carbinols Va,b at atmospheric pressure and in an autoclave (T-ble 2) shows that in this case also, the use of compressed acetylene at 95-110°C does not increase the yields of 9-vinylcarbinols VIa,b (within the limits of error of measurement of ±2%), and at 120°C the yields are even reduced by ~15%. The reaction time here was only nominally reduced to 3 h, in view of the fact that cooling of the autoclave required some days.

As will be seen from Table 2, the introduction of an additional methyl group into the 6-position of the carboline nucleus of (Vb) consistently, if only to a small extent (4-8%) increases the yields of the N-vinyl derivative (VIb. Since this methylation must reduce slightly the NH-acidity of the pyrrole moiety (as a result of the electron-donor effect of the methyl group), it would be expected that in this case the relationship between the acidity of the NH-heterocycle and its tendency to undergo base-catalyzed vinylation. In our view, however, the available information is insufficient to confirm this assumption, since the yields of VIa and VIb (the more so, since they are close to theoretical) do not provide, in the absence of quantitative measurements of the composition of the reaction mixture, a reliable measure of reactivity. The difference in yields in this instance could be due to the differing stabilities of the starting materials Va,b and the products VIa,b under the reaction conditions.

The NMR spectral parameters of the 9-vinylcarbinols VIa,b are given in Table 3. They were assigned from known data for other N-vinylpyrroles [3].

EXPERIMENTAL

The reaction mixtures were analyzed by GC on an LKhM-8MD chromatograph (catharometer detector, column 2.5 × 3 mm, 15% silicone DS-550 on Chromaton N-AW-DMCS, carrier gas helium) and TLC on unbound layers of alumina (eluent, hexane—ethanol 5:1 and hexane—ether 3:1). The IR spectra of the products were recorded on a UR-20 spectrometer as films. ^1H and ^{13}C NMR spectra were obtained on a Bruker WP-200 SY, and UV spectra on a Perkin-Elmer 402 (in ethanol).

1-Vinyl-2-(2-furyl)pyrrole (IIa). In a round-bottomed flask fitted with a mechanical stirrer, reflux condenser, thermometer, and an inlet tube for acetylene were placed 3.2 g (24 mmoles) of 2-(2-furylpyrrole) (Ia), 5.6 g (100 mmoles) of finely ground KOH, and 30 ml of DMSO. Acetylene was passed into the mixture at 100°C and atmospheric pressure for 4.5 h, and it was then diluted with water (1:2) extracted with ether, and the ether extracts washed with water and dried over potassium carbonate. After removal of the solvent, the residue was fractionated under reduced pressure to give 3.7 g (98%) of IIa, the constants of which agreed with those given in [1].

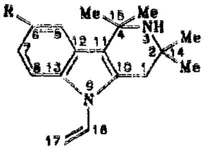
1-Vinyl-2-(2-thienyl)pyrrole (IIb). From 3 g (20 mmoles) of 2-(2-thienyl)pyrrole (Ib), 5 g (90 mmoles) of KOH, and 30 ml of DMSO at 110°C for 5 h, the other conditions being as described above, there was obtained 3.4 g (99%) of IIb, the constants of which were in agreement with those given in [1].

1-Vinyl-2-phenylpyrrole (IIc) was obtained from 0.5 g (40 mmoles) of 2-phenylpyrrole (Ic), 1 g (20 mmoles) KOH in 10 ml of DMSO at 120°C for 6 h, under the conditions described above, yield 0.57 g (96%), constants as given in [1].

N-Vinyl-4,5-dihydrobenzo[g]indole (IV). From 1 g (6 mmoles) of 4,5-dihydrobenzo[g]indole (III) in 10 ml of DMSO,with portionwise addition of 1 g (20 mmoles) of KOH (8 h, 120°C), there was obtained 1.1 g (97%) of the vinyl derivative IV, with constants as given in [1].

9-Vinyl-2,2,4,4-tetramethyl-1,2,3,4-tetrahydro-γ-carboline (VIa). In the glass apparatus described above were placed 3 g (10 mmoles) 2,2,4,4-tetramethyl-1,2,3,4-tetrahydro-γ-carboline (Va), 5 g (90 mmoles) of KOH, and 30 ml of DMSO. Acetylene was passed into the stirred reaction mixture for 6 h at atmospheric pressure. The usual workup procedure (see above) gave 3.1 g (92%) of the vinylcarboline VIa, a viscous liquid bp 172-174°C (3 mm) with a faint characteristic odor, which crystallized readily, mp 65-67°C (ethanol—water, 1:1). Found: C 80.1, H 8.8, N 10.7%. $C_{17}H_{22}N_2$. Calculated: C 80.3, H 8.7, N 11.0%.

TABLE 3. Chemical Shifts in the ^1H and ^{13}C NMR Spectra (ppm) of the 9-Vinylcarbinols VIa (R = H) and VIb (R = CH_3), 10% in $CDCl_3$, 25°C, TMS



Numbering of nucleus	VIa		VIb	
	^{13}C	^1H	^{13}C	^1H
1	37,3	2,64	37,2	2,63
2	50,7		50,7	
3		1,56		1,54
4	51,5		51,5	
5	120,4	7,58	123,0	7,36
6	121,6	7,25	129,6	
7	119,7	7,25	119,7	7,02
8	110,9	7,58	110,1	7,46
9				
10	132,5		132,5	
11	117,8		117,4	
12	126,3		126,5	
13	136,5		134,8	
14	30,8	1,27	30,7	1,26
15	31,5	1,58	31,9	1,58
16	129,6	7,00	129,7	6,98
17	102,0	4,95 5,24†	101,1	4,89 5,19†
R		7,25	21,6	2,46

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*The numbering of the nucleus is shown in the structural formula above.

†The chemical shifts of the protons in the trans- and cis-positions to the nitrogen are given respectively. The coupling constants of the protons of the vinyl moiety were 9.3 (cis-), 16.1 (trans-), and 0.7 Hz (gem-orientation).

9-Vinyl-2,2,4,4,6-pentamethyl-1,2,3,4-tetrahydro-γ-carboline (VIb). From 5.5 g (20 mmoles) of VI, 9.2 g (200 mmoles) of KOH and 60 ml of DMSO under the conditions of the preceding experiment there was obtained 6 g (99%) of Vb, mp 163°C (1 mm), mp 68-70°C (ethanol—water, 1:1). Found: C 80.7, H 9.2, N 10.4%. $C_{18}H_{24}N_2$. Calculated: C 80.6, H 9.0, N 10.4%.

The IR spectra of the 9-vinylcarbinols VIa,b contained absorption bands 3040-3020, 1640 ($CH{=}CH_2$), 2970, 2930, 2860, 1460 (CH_3), 1610 (arom. ring), and 3420-3440 cm^{-1} (associated NH). The UV spectra (c 0.5 g/liter in ethanol) contained two strong bands at 205-220 and 252-258 nm. As in indole, the first of these comprises two superimposed bands, the second being due to the N-vinyl substituent.

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