REACTION OF PHTHALIMIDONITRENE WITH PHENYLBUTENYNES

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The addition of phthalimidonitrene with phenylbutenynes proceeds exclusively at the double bond and leads to derivatives of 1-phthalimido-2-ethynylaziridine in high yield. The observed chemoselectivity of this reaction is attributed to the anti-aromatic transition state in the case of the addition of phthalimidonitrene to the triple bond.

Despite the intensive study of the reactions of aminonitrenes with olefins, dienes, and other conjugated compounds [1, 2], as well as with acetylenes [3], only a few examples have been reported for the reaction of aminonitrenes with enynes. Anderson et al. [3] reported the addition of phthalimidonitrene (III) to 2,5,5-trimethyl-1-hexene-3-yne. Recently, we carried out the addition of this nitrene to ethynycyclopentene [4]. In all cases, the reaction proceeds exclusively at the double bond. On the other hand, dichlorocarbene, which is very similar in its electronic properties of phthalimidonitrene (III) [5], may add to enynes at both the double and triple bonds and there is a strong dependence of the direction of the reaction on the nature of the substitution in the enyne fragment [6, 7], which has not yet found a strict theoretical interpretation. We only have the empirical Dehmlow rules [8], which permit the prediction of the predominant direction of the attack of dichlorocarbene.

In this regard, we carried out a systematic study of the reaction of phthalimidonitrene (III) with a series of phenylbutenynes Ia-If, in which the number and nature of the substituents in the conjugated enyne system are varied. Enynes Ib, Ie, and If were synthesized according to reported methods, while enynes Ia, Ic, and Id were obtained by the dehydration of the corresponding α-acetylenic alcohols IIa, IIc, and IId, which are readily obtained by the Iotsich reaction. However, this method, which is highly suitable for tertiary acetylenic alcohols, proved not very convenient for secondary analogs. Alcohols IIa and IIc were dehydrated only at about 200°C by the action of oxalic acid. This reaction proceeds in a complex manner and is accompanied by tar formation. The yields of products Ia and Ic were rather low. The dehydration of tertiary alcohol IId by boron trifluoride etherate gave a mixture of isomeric phenylbutenynes Id and Ig (Id was isolated as a pure compound). The sructures of the enzymes obtained were demonstrated by ^{1}H NMR spectroscopy (see Table 4) and by comparison of their indices with literature data (see Experimental).

Phthalimidonitrene (III) was generated by the oxidation of N-aminophthalimide by lead tetraacetate with binding of the acetic acid formed by potassium carbonate. Recently, doubt has been cast on the formation of free phthalimidonitrene under these conditions [9]. The formal precursor, N-acetoxyphthalimide (IV) may perform the role of nitrene III [2]. However, there is presently no unequivocal evidence to exclude the participation of nitrene III in this reaction. Thus, we will consider the addition of phthalimidonitrene (III) to enynes I although we should bear in mind that nitrenoid IV may actually be the reactive species.

In all cases, the oxidation of N-aminophthalimide in the presence of enynes Ia-If leads to the corresponding 1-phthalimido-2-ethynylaziridines Va-Vf. The products of the addition of nitrene III at the triple bond were not found. Thin-layer chromatography showed that the reaction mixtures contain only the starting enyne, the double bond adduct, which is an ordinary side product of the oxidation of N-aminophthalimide [1, 2].

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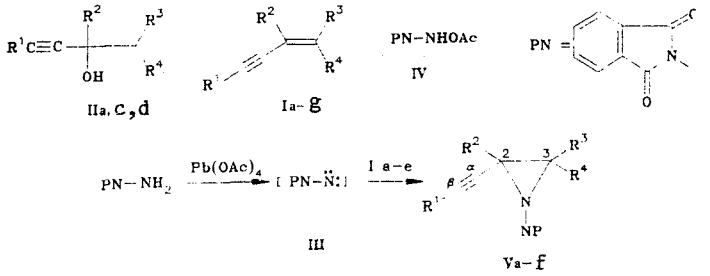


I, II, V a R^1=Ph, R^2=R^3=R^4=H; I, V b R^1=Ph, R^2=Me, R^3=R^4=H; I, II, V c R^1=Ph, R^2=H, R^3=R^4=Me; d R^1=Ph, R^2=R^3=R^4=Me; I, V e R^1=R^2=R^4=H, R^3=Ph; f R^1=R^3=Ph, R^2=R^4=H; I g R^1=Ph, R^2=*i*-Pr, R^3=R^4=H

The compositions and structures Va-Vf were supported by their melting points, elemental analysis data (Table 1), ^{1}H NMR spectroscopy (Table 2), and ^{13}C NMR spectroscopy (Table 3).* An important feature of N-aminoaziridine derivatives is the high barrier to inversion of the aziridine nitrogen atom [10, 11]. Thus, in principle, aziridines V may exist as two invertomers with syn and anti arrangement of the ethynyl substituent and the phthalimide group. Signals for both forms are seen in the NMR spectra for Va–Vd although the fraction of the minor invertomer is usually rather small. Only one set of signals is found in the spectra of phenylaziridines Ve and Vf. The assignment of invertomers to the syn and anti series was carried out by ^{1}H NMR spectroscopy (Table 2) on the basis of previous generalizations [10]: The phthalimide residue shields the syn methyl groups but, as a rule, deshields the syn protons of the aziridine ring, especially if these protons are in a cis position relative to the other unsaturated substituent.

Furthermore, the ^{1}H NMR spectra of aziridine Va–Vd and Vf clearly show the effect of the molecular geometry on the position and form of the signals of the phenyl substituent at the C≡C bond. In the anti invertomers, the ortho protons of this phenyl ring give a signal reminiscent of a doublet of doublets at about 7.5 ppm, while the meta and para protons give a multiplet at about 7.3 ppm (Va and Vc). In the syn form, the phenyl group apparently is significantly shielded by the adjacent phthalimide group (the effect of the unshared electron pair of the aziridine nitrogen atom need not be taken into consideration). As a result, all the phenyl group protons give a common multiplet at significantly higher field at 7.05-7.30 ppm centered at about 7.2 ppm. The signals of the aromatic protons of the adduct of nitrene III with 1-(2-phenylethynyl)cyclopentene described in our previous work [4] are located in this interval (7.07-7.22 ppm). The phenyl and phthalimide groups in this adduct are apparently in a syn arrangement.

The shielding effect of the phthalimide group in the ^{13}C NMR spectra (Table 3) is seen for the signals of the methyl substituents in the aziridine ring (compare these shifts for the syn and anti forms of aziridines Vb–Vd).

The equilibrium between the invertomers of N-aminoaziridines in solution at room temperature is established rather rapidly, usually in a few minutes [10]. Thus, we may consider that the ratios of the syn and anti forms of aziridines V given in Table 2 characterize their relative stability, which is clearly a function of steric factors. The interaction of the phthalimide substituent with the ethynyl group, although less favorable than with a proton, should clearly be preferable to interaction with a CH_3 group. Hence, in the case of identical substituents R^3 and R^4, aziridines Va and Vc exist largely as anti invertomers, while the syn form predominates for aziridines Vb and Vd. A phenyl group in the aziridine ring repels the phthalimide fragment even more strongly than a methyl group as indicated by the invertomer ratio in the adducts of nitrene III with methylstyrenes [10, 11]. Thus, it is not surprising that phenylaziridines Ve and Vf exist almost completely in the syn form.

1-Phthalimido-2-ethynylaziridines Va–Vf are white or yellow crystalline compounds with high solubility in methylene chloride and chloroform but reduced solubility in ether. These products are readily crystallized from hexane–ethyl acetate. With the exception of Vb, all these compounds are rather stable on silica gel. Upon chromatography on this adsorbent,

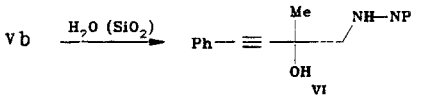
*In the assignment of the signals, we used the ^{1}H NMR spectral data for the adducts of phthalimidonitrene with the corresponding methylstyrenes [10, 11] and with 2,5,5-trimethyl-1-hexen-3-yne [3] as well as additive schemes from the work of Ionin et al. [12].

TABLE 1. Properties of 1-Phthalimido-2-ethynylaziridines Va-Vf

Compound	Chemical formula	mp, °C	Yield, %
Va	$C_{18}H_{12}N_2O_2$	172	70
Vb	$C_{19}H_{14}N_2O_2$	114...115	63
Vc	$C_{20}H_{16}N_2O_2$	132	71*
Vd	$C_{21}H_{18}N_2O_2$	125.5	74
Ve	$C_{18}H_{12}N_2O_2$	145...146 (dec.)	71
Vf	$C_{24}H_{16}N_2O_2$	116	89

*The experiment was carried out on a scale of 10 mmoles.

aziridine Vb is partially decomposed by water adsorbed on the silica gel surface with the formation of hydrazinoalcohol VI but may be recrystallized from ethanol without decomposition.



The good yields of aziridines Va–Vf with a slight excess of enyne and the small amount of phthalimide side product indicate the high reactivity of conjugated phenylbutenynes toward phthalimidonitrene (III). The direction of the reaction exclusively at the double bond is apparently the result of the circumstance that the attack of nitrene III at the C≡C bond must proceed through an antiaromatic transition state and lead initially to antiaromatic derivatives of 1H-aziridine [3], which is very unfavorable. As a consequence, even enyne If, to which dichlorocarbene adds only at the triple bond [8, 13-15], gives only the corresponding ethynylaziridine with nitrene III, while the adduct at the double bond is formed in the reaction of Ie with 1-phenylbutenyne despite the interruption of the conjugation chain in this case.

EXPERIMENTAL

The ^1H NMR spectra were taken on a Varian EM-360 spectrometer at 60 MHz, Tesla BS-567A spectrometer at 100 MHz, Bruker AC-200 spectrometer at 200 MHz, and Bruker WM-400 spectrometer at 400 MHz for solutions in $CDCl_3$ with TMS or HMDS (δ 0.05 ppm) as the internal standard. The ^{13}C NMR spectra were taken on a Bruker AC-200 spectrometer at 50.3 MHz for solutions in $CDCl_3$. The elemental analyses were carried out on a Hewlett–Packard 185B C, H, N analyzer. The gas chromatographic analysis was carried out on an LKhM-8MD chromatograph with 3 m × 3 mm glass columns packed with 5% SE-30 on Chemapol Chromatone-Super 125/160 μm and 5% OV-225 on the same support. Helium served as the gas carrier and a katharometer detector was used. The refraction indices were measured on an RDU Abbe refractor. The composition of the reaction mixtures and the purity of the compounds obtained were monitored by thin-layer chromatograph on Silufol UV-254 plates in systems of different polarity. Chemapol silica gel L 40/100 μm was used for the column chromatography. The properties of 1-phthalimido-2-ethynylaziridines Va–Vf are given in Tables 1-3, while the NMR spectral data for phenylbutenynes Ia and Ic-g are given in Table 4. The elemental analysis data for C, H, and N corresponded to the calculated values.

N-Aminophthalimide [16] and lead tetraacetate [17] were obtained according to reported procedures.

Acetylenic alcohols (IIa), (IIc), and (IId). A sample of 34 ml (0.31 mole) phenylacetylene was added dropwise to a solution of ethylmagnesium bromide prepared from 7.5 g (0.31 mole) magnesium filings, 24 ml (0.32 mole) ethyl bromide, and 120 ml ether and heated at reflux for 4 h. The reaction mixture was left overnight, heated at reflux for an additional 8 h, again left overnight. Then, a solution of 0.3 mole carbonyl compound in an equal volume of ether was added with stirring and cooling to 0-5°C. The reaction mixture was left for four days and then hydrolyzed by sat. aq. ammonium chloride. The ethereal layer was separated. The aqueous layer was extracted with four 60-ml portions of water. The ethereal solutions were combined and dried over potassium carbonate. Ether was removed at 20-30 mm. The dark oily residue was treated depending on the properties of the product.

TABLE 2. ^{1}H NMR SPectra (200 MHz) of Phenyl-Substituted 1-Phthalimidoaziridines Va–Vf, δ, ppm (J, Hz)

Compound	Form	Content, %	R^1	R^2	R^3	R^4	C_6H_4*1
Va	anti	70	7,49 m, *o*-H; 7,26...7,34 m, *m*-H and *p*-H	3,29 d.d (7,8 and 5,8)	2,87 d.d (7,8 and 1,9)	2,76 d.d (5,8 and 1,9)	7,63...7,82 m
	syn	30	7,06...7,25 m	3,31 d.d (6,2 and 5,8)	2,85 d.d (6,2 and 2,2)	3,40 d.d (5,8 and 2,2)	
Vb	anti	8	*2	1,64 s	3,11 d (2,5)	2,98 d (2,5)	*2
	syn	92	7,04...7,25 m	1,78 s	2,73 d (2,6)	3,48 d (2,6)	7,67 and 7,80
Vc	anti	94	7,47 m, *o*-H; 7,26...7,33 m, *m*-H and *p*-H	3,55 s	1,39 s	1,60 s	7,67 and 7,75
	syn	6	*2	3,32 s	1,50 s and 1,52 s		*2
Vd	anti	12	7,5 m, *o*-H*2	1,64 s*3	1,39 s	1,71 s*3	*2
	syn	88	7,16...7,31 m	1,80 s	1,53 s*3	1,60 s*3	7,64 and 7,76
Ve	syn	>98	2,31 d (2,0)	3,33 d.d (5,0 and 2,0)	7,30...7,49 m	4,36 d (5,0)	7,69 and 7,81
Vf*4	syn	>98	7,15...7,24 m	3,54 d (5,1)	7,47 m, *o*-H; 7,38 m, *m*-H; 7,34 m, *p*-H	4,46 d (5,1)	7,68 and 7,81

*1Two multiplets of the AA'BB' system, $|J_{AB} + J_{AB'}| \approx 8.5$ Hz.
*2Overlapped by signals of the major invertomer.
*3Tentative assignment.
*4Spectrum taken at 400 MHz.

TABLE 3. Chemical Shifts in the ^{13}C NMR Spectra of Phenyl-Substituted 1-Phthalimidoaziridines Va–Vf, δ, ppm

Compound	Form	Phthaloyl C atoms				Phenyl C atoms				Acetylenic C atoms		Aziridine C atoms		Methyl substituents
		C=O	C^a	C^b	C^e	*i*-C	*o*-C	*m*-C	*p*-C	α-C	β-C	2-C	3-C	
Va	anti	164,64	129,95	123,10	134,12	122,08	131,85	128,07	128,45	82,52	84,92	31,92	39,39	—
	syn	165,29	130,03	122,88	133,95	121,67	131,43	128,00	128,40	83,34	84,85	31,74	37,83	—
Vb	anti*	—	—	122,98	134,02	—	131,81	—	—	—	—	—	44,33	18,46
	syn	165,10	130,13	122,73	133,81	121,73	131,30	127,92	128,21	86,56	83,81	39,23	44,95	22,44
Vc	anti	165,34	130,11	122,71	133,80	122,48	131,56	127,88	128,13	86,61	83,92	42,30	49,28	18,88 (R^3) and 20,52 (R^4)
	syn*	—	—	122,15	133,63	—	131,3	—	—	—	—	42,11	—	24,54 (R^3) and 17,39 (R^4)
Vd	anti*	—	—	—	133,63	—	131,44	—	—	—	—	48,0	50,6	16,17 and 16,29 (R^2 and R^3); 23,47 (R^4)
	syn	165,13	130,71	122,27	133,42	122,51	131,13	127,76	127,8	86,97	85,43	45,99	52,47	20,25 (R^2); 19,54 (R^3 and R^4)
Ve	syn	165,5	129,99	122,91	133,91	134,54**	126,75	128,34	128,28	77,12	74,12	39,01	49,98	—
Vf	syn	164,82	129,77	122,62	133,76	121,38	131,22	127,86	128,06	82,71	85,27	40,20	50,52	—
						134,71**	126,87	128,23	128,23					

*A portion of the signals is overlapped by the spectrum of the major invertomer.
**Signals for the phenyl substituent in the aziridine ring.

TABLE 4. ^{1}H NMR Spectra (100 MHz) of Phenylbutenynes Ia, Ic-Ig, δ, ppm (J, Hz)

Compound	R^1	R^2	R^3	R^4
Ia	7,18...7,50 m	5,99 d.d (17,5 and 10,5)	5,48 d.d(10,5 and 3)	5,70d.d (17,5 and 3)
Ic*	7,20...7,30 m, *m*- and *p*-H; 7,30...7,47 m, *o*-H	5,46 m	1,83 br. s and 1,96 br.s	
Id	7,20...7,50 m	1,73 s, 1,85s and 1,98 s		
Ie	2,97 d (2,3)	6,01 d.d (16,5 and 2,3)	7,15...7,25 m	6,94 d (16,5)
If	7,20...7,50 m	6,32 d (16,5)	7,20...7,50 m	7,01 d (16,5)
Ig†	7,20...7,50 m	1,10 d (7); 2,47 m	5,26 d.d. (2,0 and 1,2) and 5,34 d (2,0)	

*200 MHz. The signal for 2-H is reminiscent of a distorted septet with J = 1.2 Hz.
†In a mixture with enyne Id. The protons of substituents R^2–R^4 form an $ABMX_6$ system. J_{AB} = 2 Hz, $J_{AM} = J_{AX} = J_{BX}$ = 0 Hz, J_{BM} = 1.2 Hz, J_{MX} = 7 Hz.

4-Phenyl-3-butyn-2-ol (IIa) was separated by distillation in vacuum. The yield was 20 g (45%), bp 118°C (8 mm Hg), n_D^{20} 1.5682. ^{1}H NMR spectrum (60 MHz): 1.55 (d, J = 6.5 Hz, 3H, CH_3), 4.16 (s, 1H, OH), 4.81 (q, J = 6.5 Hz, 1H, CH), 7.26 ppm (m,5H, C_6H_5). bp 79°C (0.15 mm Hg), n_D^{23} 1.5660 [18].

4-Methyl-1-phenyl-1-pentyn-3-ol (IIc) was crystallized from hexane at −60°C and washed with cold hexane. The yield was 33 g (65%). The product is a white, crystalline solid, which was shown to be pure by thin-layer chromatography and gas-liquid chromatography, mp 26°C, n_D^{26} 1.5486. ^{1}H NMR spectrum (60 MHz): 0.98 (d, J = 6 Hz, 3H, CH_3), 1.05 (d, J = 6 Hz, 3H, CH_3), 2.00 (m, 1H, CH), 3.43 (s, 1H, OH), 4.43 (d, J = 5 Hz, 1H, O–CH), 7.33 ppm (m, 5H, C_6H_5). n_D^{20} 1.5485 [19].

3,4-Dimethyl-1-phenyl-1-pentyn-3-ol (IId), $C_{13}H_{16}O$, was crystallized from hexane at −7° and washed with cold hexane. The yield was 42 g (75%). The product is a white, crystalline solid with mp 46°C, which was shown to be pure by gas-liquid chromatography. ^{1}H NMR spectrum (100 MHz): 1.04 (d, J = 6.7 Hz, 3H, CH_3), 1.08 (d, J = 6.7 Hz, 3H, CH_3), 1.88 septet, J = 6.7 Hz, 1H, CH), 2.18 (s, 1H, OH), 7.21-7.45 ppm (m, 5H, C_6H_5).

4-Phenyl-1-buten-3-yne (Ia). A mixture of 5 g (34 mmoles) alcohol IIa with 5 g oxalic acid was heated in vacuum distillation apparatus equipped with a Simroth condenser instead of an ordinary distillation column to 200°C at 20 mm Hg on a sand bath. Water at 98°C was passed through the condenser. The receiver was cooled with a mixture of salt and ice. At the end of the distillation of the product, the organic layer was separated from the organic layer, dried over potassium carbonate, and distilled in vacuum to give 0.6 g (14%), bp 70-80°C (8 mm Hg), n_D^{20} 1.5900. Gas-liquid chromatography indicated that the product contained about 15% of unidentified impurities. bp 96°C (20 mm Hg), n_D^{20} 1.6008 [20].

2-Methyl-4-phenyl-1-buten-3-yne (Ib) was prepared according to Fomina et al. [21], bp 79°C (6 mm Hg), n_D^{20} 1.5815. According to [21], bp 72-74°C (3 mm Hg), n_D^{20} 1.5820.

4-Methyl-1-phenyl-3-penten-1-yne (Ic) was obtained by analogy to enyne Ia by the dehydration of 10 g (57 mm) alcohol IIc by oxalic acid at 0.1 mm Hg. Distillation of the collected distillate in vacuum gave a product with a large amount of impurities as indicated by gas-liquid chromatography. Enyne Ic was purified by chromatography on silica gel (2.5 g mixture on 250 g sorbent) on a conical column with pentane as the eluent to give 0.8 g (9%) product with n_D^{20} 1.5825 containing about 15% unidentified impurities as indicated by gas-liquid chromatography. A much purer product sample of enyne Ic (∿95% as indicated by gas-liquid chromatography) was obtained in 20% yield by analogy with the synthesis of Ib [21] and used in the subsequent work. The product was separated by vacuum distillation, n_D^{20} 1.5890. ^{1}H NMR spectrum [15]: 1.85 br. s, 3H, CH_3), 1.96 (br.s), 3H, CH_3), 5.44 (br.s, 1H, CH), 7.10-7.45 ppm (m, 5H, C_6H_5).

3,4-Dimethyl-1-phenyl-3-penten-1-yne (Id). A sample of 6.2 ml (50 mmoles) boron trifluoride etherate was added dropwise with rapid stirring to a suspension of 18.8 g (0.1 mole)

alcohol IId in 60 ml dry hexane cooled to −15°C over 10 min and stirred for an additional 40 min at this temperature. The mixture was then poured into sat. aq. sodium carbonate. The organic layer was separated, washed with aq. sodium carbonate and water, and dried over potassium carbonate. The solvent was removed in vacuum at 20-30 mm Hg and the residue was distilled to give 5.1 g (30%) of a liquid with bp 98-102°C (0.1 mm Hg) and n_D^{20} 1.5764. Gas-liquid chromatography indicated that the distillate contained two compounds in ∿2.3:1 ratio, which were identified by ^{1}H NMR spectroscopy as isomeric enynes, namely, 3,4-dimethyl-1-phenyl-3-penten-1-yne (Id) and 2-isopropyl-4-phenyl-1-buten-3-yne (Ig), respectively. The mixture was separated on 350 g silica gel on a conical column with pentane as the solvent to give 2.02 g (13%) of enyne Ig with n_D^{20} 1.5835, which was shown to be a pure sample by gas-liquid chromatography. Enyne Ig could not be isolated as a pure compound.

E-1-Phenyl-1-buten-3-yne (Ie) was synthesized according to Lötzberger [22], bp 64°C (2 mm Hg), n_D^{20} 1.6158. This sample was found to be pure according to gas-liquid chromatography. Bp 45°C (0.3 mm Hg) [22].

E-1,4-Diphenyl-1-buten-3-yne (If) was obtained according to Straus [23] from 12 g (0.12 mole) phenylacetylene. This sample was found by thin-layer chromatography to be a mixture of two compounds with similar R_f using pentane as eluent. The mixture was separated on 500 g silica gel on a conical column with hexane as eluent. A portion of the mixture remained unresolved. Only 1.3 g (11%) diphenylbutadiyne and 2.3 g (19%) enyne If were isolated. The compositions and structures of these products were supported by elemental analysis and ^{1}H NMR spectroscopy. E-1,4-Diphenyl-1-buten-3-yne (If), $C_{16}H_{12}$, mp 95°C (from ethanol). mp 96.5-97°C [23]. Diphenylbutadiyne, $C_{16}H_{10}$, mp 79-80°C (from methanol). Thin-layer chromatography and ^{1}H NMR spectroscopy indicate an impurity of enyne If. mp 87°C [24].

1-Phthalimido-2-ethynylaziridines (Va)-(Vf). A sample of 5 mmoles dry lead tetraacetate was added with stirring in small portions over 10-15 min to a suspension of 5 mmoles N-aminophthalimide and 20 mmoles potassium carbonate in 30-50 ml anhydrous distilled methylene chloride containing 5.5-6.0 moles enyne Ia–If cooled to from −10 to −20°C. This mixture was stirred for 30-60 min at this temperature and filtered through a layer of silica gel. The residue on the filter was washed with methylene chloride until the filtrate was colorless. The filtrate was evaporated in vacuum using a water pump and the solid residue was washed with pentane or hexane to remove the unreacted enyne. Adducts Va–Vf were obtained as pure compounds as indicated by ^{1}H NMR spectroscopy and thin-layer chromatography. For the elemental analysis and melting point determination, the samples of Va and Vc–Vf were recrystallized from ethyl acetate–hexane, while aziridine Vb was recrystallized from ethanol.

2-Methyl-4-phenyl-1-(2,2-phthaloylhydrazino)-3-butyn-2-ol (VI) was separated in an attempt to effect the chromatographic purification of aziridine Vb on silica gel, mp 112-113°C (from ethanol). ^{1}H NMR spectrum (200 MHz): 1.56 (s, 3H, CH_3), the CH_2NH form an ABX system, in which the X part corresponds to the NH proton, δ_A 3.65, δ_B 2.98, δ_X 4.88 ppm, J_{AB} = 13.0 Hz, J_{AX} = 4.3 Hz, J_{BX} = 5.0 Hz, 4.44 (s, 1H, OH), 6.9-7.1 (m, 5H, C_6H_5), 7.60 and 7.76 ppm are multiplets of the AA'BB' system, which is formed by the phthalimide group protons, $|J_{AB} + J_{AB'}|$ = 8.5 Hz.

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SYNTHESIS AND SPECTRAL PROPERTIES OF 1-ARYL-2-FORMYLPYRROLES

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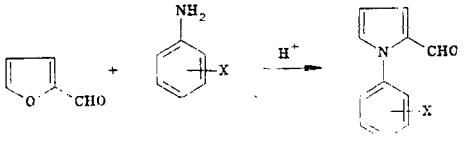
Various 1-aryl-2-formylpyrroles were synthesized by reaction of furfurol with substituted anilines. For p-bromo- and p-chlorophenylsubstituents, the intermediate Schiff bases were isolated.

Recently it was shown that in contrast to the Yur'ev reaction conditions [1], 1-(p-nitrophenyl)-2-formylpyrrole can be synthesized from furfurol under mild conditions with 70% yield [2]. This work extends that synthetic method to other 1-arylpyrroles.

The reaction of furfurol with aromatic amines is known to occur differently depending on the conditions [3, 4]: in acidic media, besides the pyrrole derivatives, the formation of pyridine salts is possible [3, 5], the acidity of the medium having a significant role [2]; in neutral media, cyclopentenones are formed [5]; and the nature of the substituent on the benzene ring of the amine also is important [6].

We found the optimal conditions for synthesis of p- and m-nitrophenyl-2-formylpyrroles at a ratio of pyrrole:amine:acid of 1:2:1. The purity of the starting materials and the constant addition of acid to the reaction mixture are important.

Application of the conditions to other anilines showed that in spite of a decrease in nucleophilicity, the best results are obtained for anilines with acceptor substituents (Table 1).



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