FORMATION OF FREE RADICALS IN THE VINYLATION OF 2-SUBSTITUTED PYRROLES WITH ACETYLENES IN A KOH—DMSO SYSTEM

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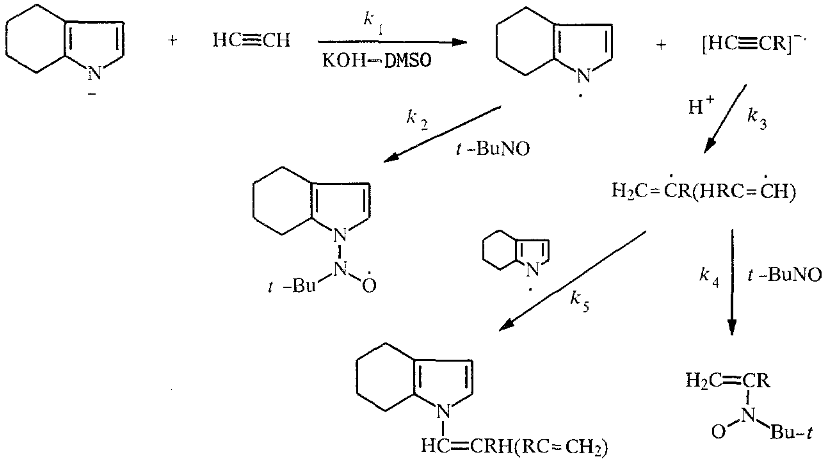
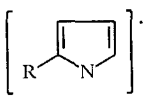
By spin trapping, using 2-methyl-2-nitrosopropane (t-BuNO), the EPR signals of vinyl-tert-butylnitroxyls and spin adducts of t-BuNO with products of the addition of 2-substituted pyrrole radicals to acetylenes were recorded during the vinylation of 2-substituted pyrroles with acetylenes in a KOH—DMSO system. The 2-substituted pyrrole radicals have a high stability, and their EPR spectra were observed directly in the vinylation reactions. It is shown that one-electron transfer processes are involved in vinylation.

Earlier, using the spin-trapping technique, we carried out an EPR study of the vinylation of tetrahydroindole with acetylene and phenylacetylene in a superbasic medium (KOH—DMSO) [1]. It was shown that in this case the spin trap, 2-methyl-2-nitrosopropane (t-BuNO) not only captures aminyl radicals but, to some degree, itself oxidizes the tetrahydroindole anions, giving an additional quantity of tetrahydroindole radicals. This shows that the redox potentials of tetrahydroindole anion and the spin trap differ by little more than 0.2 V [2, 3]. It was not possible in this case to detect spin adducts of t-BuNO with vinyl radicals. Possibly, the rate constants for the acceptance of a tetrahydroindole radical by the trap (k_2) and the addition of a vinyl radical to a tetrahydroindole radical (k_5) are much larger than the rate constant for the trapping of a vinyl radical by the trap (k_4).



In the present work, the study of the radical processes in the vinylation of pyrroles in the KOH—DMSO system is continued. The 2-substituted pyrroles 2-phenylpyrrole (I), 2-(4-chlorophenyl)pyrrole (II), 2-(4-methylphenyl)pyrrole (III), 2-furylpyrrole (IV), and 2-thienylpyrrole (V) are vinylated under the conditions in [1] with no notable differences. During the vinylation of 2-arylpyrroles I-III in the presence of t-BuNO, however, several other radicals were detected (Table 1) than in the vinylation of tetrahydroindole. During the vinylation of compounds IV and V, no spin adducts were observed at all. It should be emphasized that in none of the cases were the captured spin traps the expected, nitrogen-centered radicals of 2-arylpyrroles



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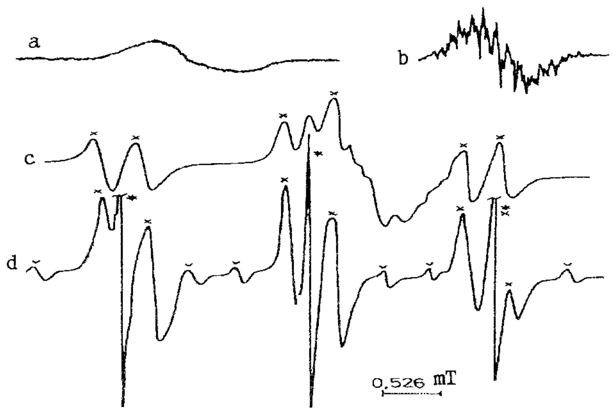

Fig. 1. EPR spectra observed during the vinylation of 2-phenylpyrrole: a) with phenylacetylene in the absence of the spin trap; b) with acetylene in the presence of the spin trap under high resolution (central portion of spectrum); c) with phenylacetylene in the presence of the spin trap 1 h after the start of the reaction; and d) after 3 h. Lines belonging to a single adduct are labeled with the same sign; *) di-tert-butyl-nitroxyl lines.

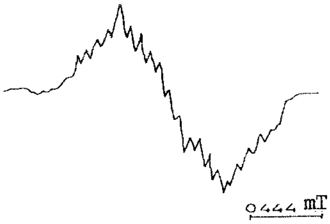

Fig. 2. EPR signal recorded in the 2-phenylpyrrole–KOH–DMSO system.

TABLE 1. Characteristics of the EPR Signals of the Spin Adducts Recorded during the Vinylation of Pyrroles

Pyrrole	Phenylacetylene			Acetylene *		
	nature of the splitting	HFC [hyperfine coupling] constants, mT		nature of the splitting	HFC [hyperfine coupling] constants, mT	
		a_N	a_H		a_N	a_H
I	$^3N \times {}^2H$	1,500	0,333	$^3N \times {}^2H$	1,289	1,022
	$^3N \times {}^2H$	1,566	1,222	$^3N \times {}^2H$	1,622	1,244
II	$^3N \times {}^2H$	1,511	0,289	$^3N \times {}^2H$	1,178	1,178
	$^3N \times {}^2H$	1,566	1,222	$^3N \times {}^2H$	1,622	1,244
III	$^3N \times {}^2H$	1,466	0,373	$^3N \times {}^2H$	1,155	1,155
	$^3N \times {}^2H$	1,566	1,222	$^3N \times {}^2H$	1,622	1,244

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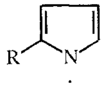
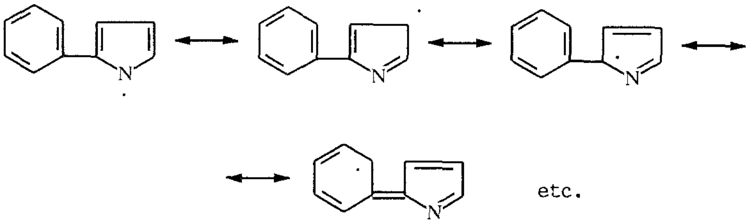
*A nitrogen triplet with a constant of 1.422 mT (not identified) was also observed in the spectrum.

Unlike tetrahydroindole, the 2-substituted pyrroles I-V during vinylation without a spin trap show a singlet in the EPR spectrum in the 2.0036-2.0042 region of g-factors (Fig. 1a) with a width of ~0.6-0.7 mT. This same signal is also observed during reactions in the presence of t-BuNO and, depending on conditions (vacuum, inert atmosphere) can be resolved to some degree (Figs. 1b and 2).

In the literature, cases are described of electron transfer onto a carbon triple bond from anions [4], and also in reactions of alkali metals with acetylene in a low-temperature matrix [5] to form anion radicals. However, it is not possible to record directly the EPR spectra of acetylenic anion radicals under the conditions in which the vinylation of the pyrrole derivatives takes place. Therefore, the lone signal cannot be assigned to acetylenic anion radicals. Since the nature of the HFC of the signals suggests the participation of several magnetic nuclei in the hyperfine interaction (see Figs. 1b and 2), we were at first inclined to assign it to paramagnetic oligomers of acetylene and phenylacetylene [6, 7] or to radical adducts of the 2-substituted pyrroles with the acetylenes. A more detailed study showed that this signal is most probably to be assigned to free radicals forming from pyrroles I-V in the KOH—DMSO system (see Fig. 2). The g-factor values on the order of 2.004 (see Table 1) are characteristic of aminyl radicals [8]. The addition to this system of acetylenes leads to some reduction of the steady-state intensity of the EPR signal (in the presence of the spin trap, the reduction of the intensity is substantially retarded). Thus, the lone signal with unresolved HFC can be assigned to 2-substituted pyrrole radicals.

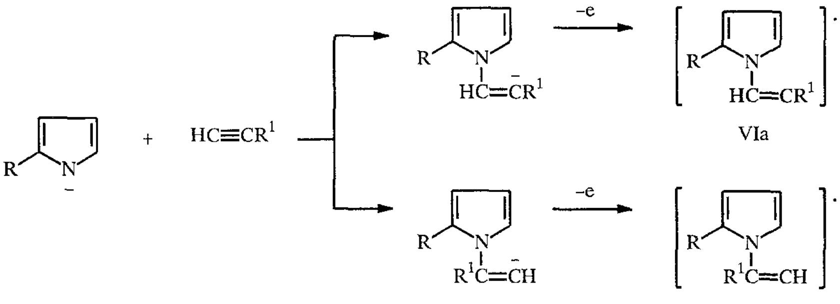


Apparently, these radicals are not captured by the spin trap because of their relative stability arising from the redistribution of spin density and also for steric reasons.



In the KOH—DMSO—2-substituted pyrrole system the trap t-BuNO does not trap the free radicals at all.

Take the assumptions that the spin adducts of t-BuNO with 2-substituted pyrroles are significantly less stable than the corresponding adduct with 4,5,6,7-tetrahydroindole, or that the steric factors in the 2-substituted pyrrole radicals are substantially greater than in the tetrahydroindole radical to be unfounded. Since the tetrahydroindole radical itself is not observed in the EPR, and the 2-substituted pyrroles are extremely stable, the assumption remains that all of the observed effects are determined by the ratios of the rate constants of the addition of the pyrroles to the acetylenes and of the trap to free radicals of type VI based on anionic intermediates.



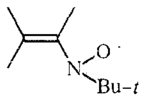
VIa

VI b

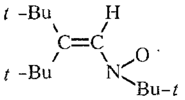
The 2-arylpyrroles, being rather stable radicals, react with the acetylenes considerably more slowly than do the slightly stable tetrahydroindole. However, in 2-substituted pyrrole—acetylene (phenylacetylene)—KOH—DMSO—t-BuNO systems, spin adducts of the trap with the radicals being formed are recorded only for 2-arylpyrroles I-III.

The EPR spectra of the spin adducts for compounds I-III are superpositions of two triplets of doublets and, in the case of vinylation with acetylene, an additional nitrogen triplet with a constant of 1.422 mT (Table 1).

In order to assign the signals observed, we analyzed the existing literature data on the preparation and study of vinylnitroxyl radicals [9-12]. Attempts to prepare vinylnitroxyl radicals have been undertaken repeatedly [9-11]. Most often, they proved unsuccessful, although in a series of experiments weak EPR signals attributed to

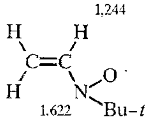


were obtained, for which the nitrogen constant varied in the range 12.5-13 Gs (1.25-1.3 mT) [12]. The authors note the unexpected fact that still only one C_α proton interacts with the unpaired electron. A triplet of doublets was recorded for the radical

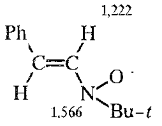


with constants of 11.1 Gs (1.11 mT) for the nitrogen atom and 10.3 Gs (1.03 mT) for the proton [10]. That is, depending on the steric factors, the constants in vinylnitroxyl radicals can vary over a rather broad range, and the proton constant, in particular, varies widely from 3.6 to 13.6 Gs (from 0.36 to 1.36 mT) [10].

From what has been said, one of the EPR signals recorded during the vinylation of 2-arylpyrroles with acetylenes in the presence of 2-methyl-2-nitrosopropane can obviously be assigned to vinyl-tert-butylnitroxyls VII, VIII.

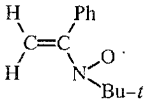


VII



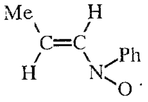
VIIIa

or



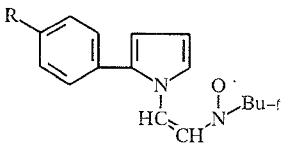
VIIIb

Of the two possible spin adducts, VIIIa and VIIIb, of the phenylacetylene radicals, structure a is preferred since a splitting corresponding to the p-, o-, and m-protons of the phenyl substituent should be observed for structure b. In addition, calculations by the McLachlan method for the



radical show that the splitting constant at the C_α proton should be no less than 13 Gs (1.3 mT) [10].

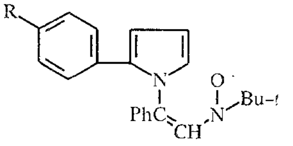
The following structures can apparently be ascribed to the second spin adduct detected in the vinylation of 2-arylpyrroles with acetylenes:



IX

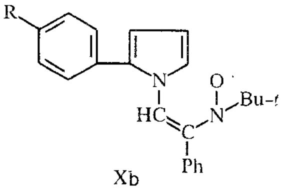
R	^{a}N, mT	^{a}H, mT
H	1,289	1,022
Cl	1,178	1,178
Me	1,155	1,155

and



Xa

or

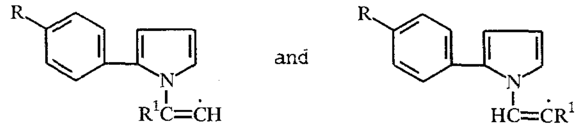


Xb

R	^{a}N, mT	^{a}H, mT
H	1,500	0,333
Cl	1,511	0,289
Me	1,466	0,373

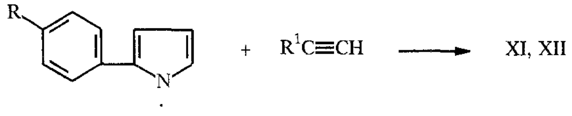
Of the two possible structures Xa and Xb, the latter is obviously the preferred one, and the doublet constant on the order of 0.3 mT is assigned to the p-proton of the phenyl group [9] since the splitting at the α-H proton must be substantially greater, judging from the data in [10].

The formation of radicals



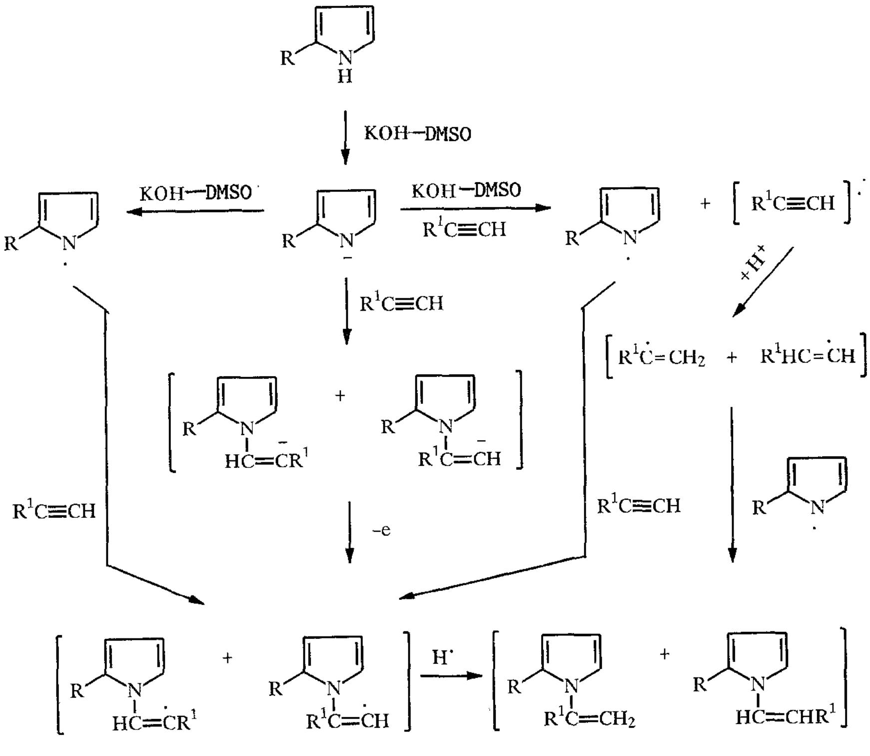
R=H, Cl, Me; R^1=H, Ph

can be explained (apart from the oxidation of the intermediate anions; see above) by the addition of aminyl radicals to the acetylenes



$$\text{XI, XII} \xrightarrow{t\text{-BuNO}} \text{IX, X}$$

The fact that the spin trap does not trap any radicals during the vinylation of pyrroles IV and V under analogous conditions, together with the fact that in the presence of the spin trap the intensity of the EPR signal from the aminyl radicals is increased, shows that the difference in the redox potentials of the trap and radical is less than 0.2 V, and the addition of the radical to the trap cannot compete with the electron transfer reaction.



R = Ar; R^1 = H, Ph

Thus, to summarize, proceeding from the structure of the trapped radicals, the vinylation of 2-arylpyrroles can be mirrored by the indicated mechanism. Anions of type VI can be oxidized to radicals by dimethylsulfoxide or 2-methyl-2-nitrosopropane, or by an electron transfer to acetylene.

EXPERIMENTAL

The EPR spectra were recorded on RÉ-1307 and EKh-2547 spectrometers (Radiopan). The reactions of compounds I-V with acetylene and phenylacetylene in a KOH—DMSO system were carried out at ~20°C directly in the resonator of the

EPR spectrometers in special cells of two kinds allowing acetylene or argon to be passed through them. Compounds I-V were sublimed immediately before an experiment. Phenylacetylene was purified by distillation, also immediately before an experiment (bp 142°C, purity 100%, GLC analysis). In order to remove water and acetone impurities, the acetylene was passed through a coiled trap cooled to —70°C at a rate of 100 ml/min. Concentrations of KOH, pyrroles I-V, phenylacetylene, and spin trap (2-methyl-2-nitrosopropane) were 0.86, 0.43-0.47, 0.86, and 0.05-0.2 M, respectively. In the case of acetylene, a saturated solution of it in the reaction mixture at atmospheric pressure was obtained. Under the experimental conditions the spin trap itself did not give EPR signals in the KOH—DMSO system.

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