PROPERTIES OF A MULTIPLE BOND CONJUGATED WITH A PYRIDINE RING

IX * REACTION OF VINYLPYRIDINES WITH PIPERYLENE AND ISOPRENE

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The composition of the products of the reaction of 2-vinylpyridine (I), 4-vinylpyridine (II), and 2-methyl-5-vinylpyridine (III) with piperylene and isoprene as well as the composition of catalysates obtained by dehydration of the isolated adducts were studied by means of gas-liquid chromatographic analysis. The reaction of I-III with isoprene forms only one 1,4-isomeric adduct, which gives the corresponding p-tolylpyridine on dehydrogenation. The reaction of I-III with piperylene, however, forms a mixture of 1,2- and 1,3-isomeric adducts, which give a mixture of the corresponding m-tolylpyridines on dehydrogenation; nation; in the case of I, the 1,2-isomer predominates in the mixture, while the 1,3-isomer predominates in the reaction with II and III.

In a previous investigation [1] of this series we showed that vinylpyridines are active dienophiles in the reactions with oxazoles. Of the two possible orientations of the vinylpyridine with respect to the unsymmetrical diene, only one is generally realized. 3-Ethynylpyridine also gave only one of the two possible isomeric pyridylpyrazoles in 1,3-dipolar addition reactions [2]. It was of interest to verify whether this rule extends itself to the reaction of vinylpyridines with unsymmetrical diene hydrocarbons.

This reaction has been discussed several times in the literature, and it was found [3-5] that 2-vinylpyridine (I) and 4-vinylpyridine (II) are somewhat more reactive, while 3-vinylpyridine is equal in activity to styrene in 1,4-cycloaddition reactions.

The literature indicates that only one of the possible structural isomers is formed in the reaction of vinylpyridines with such unsymmetrical dienes as piperylene and isoprene. In fact, only the corresponding o-tolylpyridines were detected in the reaction mixture (after its dehydrogenation over palladium) in the reaction of I and II with piperylene, while only p-tolylpyridines were detected in the reaction of the same vinylpyridines with isoprene [5]. In addition, it is well known that both possible structural isomers (1,2- and 1,3-) were isolated in a ratio of 6 : 1 in the reaction of styrene, for example, with piperylene [6-7].

We have studied the diene reaction of isomeric vinylpyridines I and II and 2-methyl-5-vinylpyridine (III) with piperylene and isoprene by investigating the composition of the reaction products by means of gas-liquid chromatography. The analysis was carried out before and after rectification of the reaction mixture, during which the analytical data for both the reaction mixture and the isolated fractions did not differ significantly.

The adduct fractions obtained were dehydrogenated over palladium, and the composition of the catalysates obtained was also determined by means of gas-liquid chromatography.

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*See [2] for Communication VIII.

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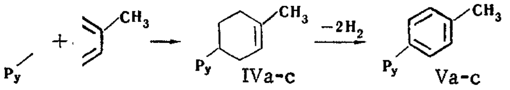
TABLE 1. Overall Yields and Chromatographic Characteristics of Adducts of Vinylpyridines with Isoprene and Their Dehydrogenation Products

Compound	T_{adj}, min	V, ml	Yield, %
IVa	22	1100	53
IVb	36	1800	49
IVc	37	1850	60
Va	66	3300	72
Vb	69	3450	82
Vc	73	3650	70

Our investigations established that the yields of the adducts of the isomeric vinylpyridines with both piperylene and isoprene are only slightly dependent on the position of the vinyl group in the pyridine ring. Nevertheless, we also found that III was a little less reactive than I and II.

In the gas-liquid chromatographic analysis of the isoprene adducts with all three vinylpyridines we always obtained one peak on the chromatogram. Moreover, while the retention times (T) and retention volumes (V) for the adducts with II (IVb) and III (IVc) were close, they were considerably lower for the adduct with I (IVa) (see Table 1).

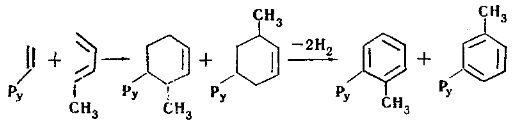


IVa-c Va-c

Py = a) 2-pyridyl b) 6-methyl-3-pyridyl c) 4-pyridyl

The isomeric tolylpyridines were obtained after dehydrogenation of the adducts, and the constants of 2- (Va) and 4-tolylpyridine (Vc) were in agreement with the literature data. The mass-spectral characteristics and the character of the decomposition of the 2-methyl-5-tolylpyridine (Vb) obtained were analogous to the mass-spectral behavior of Va and Vc, on the basis of which we also assigned the 2-methyl-5-(p-tolyl)pyridine structure to it.

Thus the literature data on the structural selectivity of the reaction of vinylpyridines with isoprene were confirmed in our study. However, two peaks (see Fig. 1) with an area ratio of 3 : 1 were obtained by gas-liquid chromatographic analysis of the adduct of I with piperylene, and the product of aromatization of this adduct also contained two compounds, viz., 2-(o-tolyl)pyridine (VIII a) and 2-(m-tolyl)pyridine (IXa) in approximately the same ratio. This indicated that the two compounds in the adduct can only be structural isomers VIa and VIIa.



VIa-c VIIa-c VIIIa-c IXa-c

In assigning the peaks in Fig. 1 to a definite compound we allowed for the fact that the T and V values for IVa, which is, as we established, pure "para adduct", were considerably larger than those for the peaks found; this could be explained by the minimum steric hindrance of the IVa molecule. In this case, T_{VI} (V_{VI}) should be less than T_{VII} (V_{VII}), and T_{VIII} (V_{VIII}) < T_{IX} (V_{IX}). In fact, the peak that we assigned to VIIIa on the basis of the above discussion coincided with the peak of pure, synthetic 2-(o-tolyl)pyridine,* which confirmed the correctness of the peak assignments.

The chromatograms of the products of the reaction of piperylene with II and III were more complex and, in addition to the peaks for the two major compounds, had additional peaks that were poorly separated from the major peaks. These peaks apparently corresponded to secondary steric isomers (cis or trans) of each of the structural isomers since the catalysates obtained by aromatizations of these adducts contained only two isomeric tolylpyridines (ortho and meta). The percentage composition and chromatographic

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*Compound VIIIa was synthesized by the method described in [8].

TABLE 2. Composition* and Chromatographic Characteristics of the adducts of Vinylpyridines with Piperylene (VI and VII) and Their Dehydrogenation Products (VIII and IX)

Compound	Percentage in mixture	T_{adj}, min	V, ml
VIa	75	13	650
VIIa	25	16	800
VIb	32	22	1180
VIIb	68	28	1400
VIc	35	23	1250
VIIc	65	29	1450
VIIIa	67	32	1600
IXa	33	45	2250
VIIIb	75	37	2000
IXb	25	53	2900
VIIIc	64	37	2000
IXc	36	55	2980

*The sum of the cis and trans isomers is given for VI and VII.

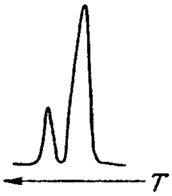

Fig. 1. Chromatogram of the products of the reaction of 2-vinylpyridine (I) with isoprene.

characteristics of the adducts with piperylene and their dehydrogenation products are presented in Table 2.

It is apparent from the data in Table 2 that the reaction of vinylpyridines with piperylene does not proceed completely specifically with respect to structure; while the major component in the mixture from the reaction of piperylene with I is the 1,2 isomer (VIa), the 1,3 isomers (VIIb and VIIc) are formed in large quantities in the reaction with II and III.

However, the percentage of 1,2 isomer in the products of dehydrogenation of the adducts obtained increases, which indicates the different rates for their dehydrogenation. It is perhaps precisely this that served as a basis for the erroneous opinion in the literature that the 1,2-isomer predominates in the reaction of piperylene with vinylpyridines.

The elevated percentage of the "ortho-isomeric" adduct observed in the case of the reaction of I with piperylene should apparently be explained by the proximity of the nitrogen atom to the reacting multiple bond, which promotes stabilization of the transition state.

EXPERIMENTAL

Gas-liquid chromatographic analysis was carried out with a "Tswett" chromatograph with a 3-m long column on diatomaceous brick (TND-TS-M, 40-50 mesh), impregnated with polyethylene glycol (m-1500, 15 wt. %) at 200 deg and a gas-carrier flow rate (helium) of 50-54 ml/min. The reaction of I and II with piperylene and isoprene was accomplished by heating equimolecular amounts of the components in xylene in a sealed ampule for 12 h at 170-175 deg. The resulting adducts were dehydrogenated by passage in a nitrogen stream into a catalytic furnace at 300-310 deg over palladium on carbon.

The constants of IVa and b and Va and c and of mixtures of VIa,c + a,c and VIIIa,c + IXa,c were in agreement with the literature data [5].

4-(6-Methyl-3-pyridyl)-1-methyl-1-cyclohexene (IVb). A solution of 14 ml (0.11 mole) of 2-methyl-5-vinylpyridine and 12 ml (0.17 mole) of isoprene in 40 ml of xylene was heated in a sealed ampule at 175-180 deg for 36 h. The xylene was removed by distillation, and the residue was vacuum distilled to give 10.0 g (49%) of a product with bp 134-135 deg (7 mm) and n_D^{20}1.5375. The picrate had mp 186-187 deg (from alcohol). Found %: C 55.09, 55.01; H 5.10, 5.06; N 13.67, 13.79. $C_{19}H_{20}N_4O_7$. Calc. %: C 54.80; H 4.80; N 13.70.

2-Methyl-5-(p-tolyl)pyridine (Vb). Compound IVc (7.5 g) was passed in a nitrogen stream into a catalytic furnace over 7 g of 20% palladium on carbon at 300 deg. The catalysate (6.7 g) obtained was dissolved in ether, and the solution was dried with anhydrous magnesium sulfate. The solvent was removed, the unchanged IVc was removed by vacuum distillation, and the crystalline residue was recrystallized to give 82% (based on converted IVc) of a product with mp 94-95 deg (from hexane). Found %: C 85.00, 84.97; H 7.34, 7.40; N 7.49, 7.64; $C_{13}H_{13}N$. Calc. %: C 85.16; H 7.18; N 7.85. The picrate had mp 194-195° (from alcohol).

Adduct of III with Piperylene (VIb + VIIb). A solution of 4.6 g (0.038 mole) of III and 4 ml (0.04 mole) of piperylene in 20 ml of xylene was heated in a sealed ampule at 175-180 deg for 36 h. The xylene was removed by distillation, and the residue was vacuum distilled to give 3.2 g (50.5%. based on converted III) of a product with bp 136-137 deg (13 mm) and n_D^{20} 1.5375. The picrate had mp 158-159 deg (from alcohol). Found %: C 54.71, 54.97; H 5.05, 4.98; N 13.47, 13.46. $C_{19}H_{20}N_4O_7$. Calc. %: C 54.80; H 4.80; N 13.70.

Mixture of 2-Methyl-5-(o-tolyl)piperidine (VIIIb) and 2-Methyl-5-(m-tolyl)pyridine (IXb). The adduct described above (3.0 g) was dehydrogenated over palladium on carbon at 300 deg to give 0.9 g (53%, based on converted adduct) of a product with bp 157-158 deg (20 mm) and n_D^{20} 1.5723. The picrate had mp 163-164 deg (from alcohol). Found %: C 54.98, 55.15; H 4.14, 4.07; N 13.83, 13.60. $C_{19}H_{16}N_4O_7$. Calc. %: C 55.30; H 3.93; N 13.60.

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