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1,4-CYCLOADDITION OF 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE TO 2-VINYLPYRIDINES

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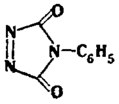
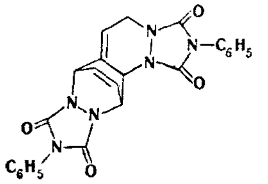
The addition of 4-phenyl-1,2,4-triazoline-3,5-dione (I) to the pseudodienic system of 2-vinylpyridines leads to a new heterocyclic system – triazolo[1,2-*a*]-5-azacinnoline. A second molecule of I undergoes further reaction of the substitutive addition type.

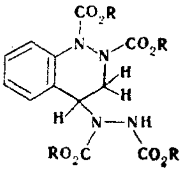
It is well known that styrene, because of its pseudodienic system, which is formed by the vinyl group and the aromatic ring double bond conjugated with it, is capable of reacting with active dienophiles via a 1,4-cycloaddition scheme [1,2]. In the reaction of styrene and its analogs with 4-phenyl-1,2,4-triazoline-3,5-dione (I), two molecules of the latter undergo reaction, and the product has structure II. Styrene reacts differently with azodicarboxylic acid esters, and adduct III is formed [2].



I



II



III

We have investigated the behavior of 2-vinylpyridine and its derivatives in the reaction with dienophile I. The bright color of 4-phenyl-1,2,4-triazoline-3,5-dione vanishes after a few minutes in ether at room temperature, and colorless amorphous adducts with compositions corresponding to the addition of two molecules of dienophile I to one molecule of vinyl pyridine are formed in 60-80% yields.

In contrast to styrene, 2-vinylpyridines react with I with retention of the aromatic character of the pyridine ring. Compounds with structure IV are formed in this case, as is shown in the scheme at the top of the next page.

Evidence in favor of this structure is offered by the presence of an intense absorption band of an NH group at 3180-3190 cm^{-1}, which cannot be present in the spectrum in the case of structure II. In addition, the chemical shifts of the signals of the protons in the aromatic region (in addition to the signals of the two C_6H_5 groups), their multiplicities, and the J constant are characteristic for the protons of the pyridine ring [3](see Table 2). For example, quartets of 9-H protons at δ 9.4 ppm ($J_{98} = 9$ Hz, $J_{97} = 1.5$ Hz), 7-H at δ 8.57 ppm ($J_{78} = 4.5$ Hz, $J_{79} = 1.5$ Hz), and 8-H at δ 8.03 ppm ($J_{87} = 4.5$ Hz, $J_{89} = 9$ Hz) are observed for IVa. In the case of structure II one should have expected the presence of signals of olefinic protons at stronger field. It is characteristic that, in contrast to compounds of the

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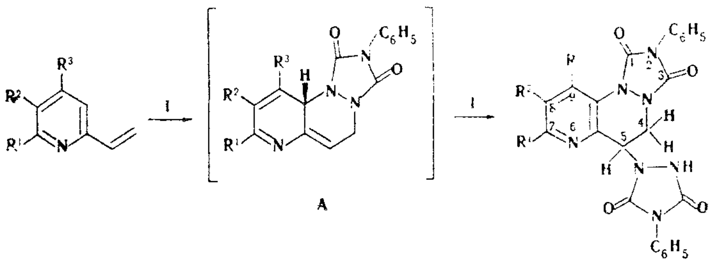
M. V. Lomonosov Moscow State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 702-705, May, 1976. Original article submitted April 28, 1975.



IV a–e

IV a $R^1=R^2=R^3=H$; b $R^1=CH_3$, $R^2=R^3=H$; c $R^1=R^3=H$, $R^2=CH_3$; d $R^2=C_2H_5$, $R^1=R^3=H$; e $R^1=R^2=H$, $R^3=CH_3$

pyridine and quinoline series, the 9-H proton lies at weaker field than the 7-H proton; this is evidently explained by the anisotropic effect of the closely located carbonyl group (attached to C_1).

In addition to low-intensity molecular ion peaks (10%), the mass spectra of IV contain M — HNCO fragment-ion peaks and peaks of ions corresponding to the loss of a phenylurazole fragment by the molecular ion, whereas for compounds with structure II one should expect a different fragmentation pathway — loss of C_6H_5NCO, CO, and N-phenyltriazolinedione I molecules. At the same time, the molecular ion with structure II should not eliminate HNCO and phenylurazole fragments.

TABLE 1. Properties of IVa–e

Compound	R^1	R^2	R^3	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
						C	H	N	C	H	N	
IV a	H	H	H	233—235	$C_{23}H_{17}N_7O_4$	60,5	3,7	21,4	60,7	3,7	21,5	85
IV b	CH_3	H	H	240—241	$C_{24}H_{19}N_7O_4$	61,3	4,0	—	61,4	4,1	—	80
IV c	H	CH_3	H	209—210	$C_{24}H_{19}N_7O_4$	61,3	4,0	20,7	61,4	4,1	20,9	80
IV d	H	C_2H_5	H	210—212	$C_{25}H_{21}N_7O_4$	61,9	4,3	20,2	62,1	4,4	20,3	75
IV e	H	H	CH_3	200—204	$C_{24}H_{19}N_7O_4$	—	—	20,7	—	—	20,9	60

TABLE 2. PMR, UV, IR, and Mass Spectra of IVa–e

Compound	PMR spectra, ppm				UV spectra λ_{max}, nm (log ε)	IR spectra, cm^{-1}	Mass spectra*, m/e (%)
	7-H	8-H	9-H	CH_3			
IV a	8,57	8,03	9,4	—	260 (4,28) 315 (3,54)	1700—1740, 1790, 3190	455 (5), 412 (2), 319 (17), 293 (13), 279 (19), 177 (10), 172 (22), 161 (11), 160 (14), 146 (30), 133 (42)
IV b	—	7,97	9,33	7-CH_3 2,90	265 (4,30) 317 (3,57)	1710—1730, 1795, 3190	469 (29), 426 (6), 333 (37), 322 (31), 307 (18), 294 (70), 293 (41), 292 (45), 186 (11), 147 (45), 133 (15)
IV c	8,57	—	9,37	8-CH_3 2,62	252 (4,27) 265 i† (4,18) 314 (3,57)	1705—1730, 1790, 3185	469 (5), 426 (2), 333 (80), 322 (4), 307 (24), 293 (14), 186 (68), 160 (44), 147 (28), 136 (16), 133 (8)
IV d	8,55	—	9,35	8-CH_2 3,08	252 (4,28) 267 i (4,16) 313 (3,51)	1700—1730, 1790, 3190	483 (6), 440 (3), 347 (76), 321 (34), 308 (12), 307 (16), 306 (12), 200 (80), 174 (76), 161 (34), 144 (24), 131 (18)
IV e	8,56	8,00	—	9-CH_3 2,74	268 (4,26) 316 (3,53)	1700—1740, 1795, 3195	469 (3), 426 (1), 307 (7), 293 (11), 191 (3), 186 (7), 175 (2), 174 (2), 147 (13), 145 (14)

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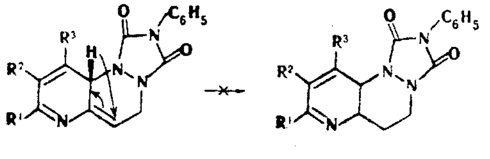
*The most intense ion peaks are presented (the maximum peak for all of the compounds was that of the ion with m/e 119.

†An inflection is indicated by the letter "i".

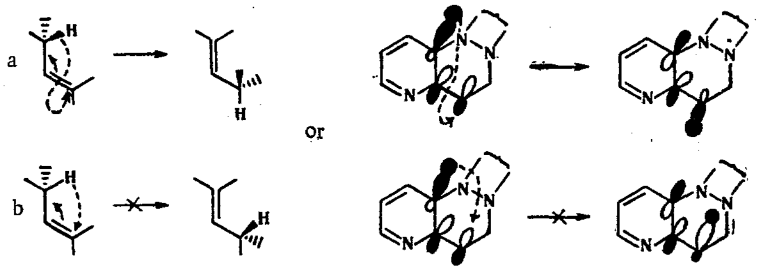
The first step in the reaction for both styrene and 2-vinylpyridine is evidently 1,4-cycloaddition to give an intermediate of the A type. However, whereas for styrene the new dienophile molecule reacts with the diene system of intermediate A to give structure II, the more passive heterodienic system of the vinylpyridine intermediate with a nitrogen atom at the end hinders diene synthesis, and the reaction proceeds in a different direction to give IV.

In addition, possible isomerization via the A→V scheme also does not occur.



A V

According to the Woodward—Hoffman concept, this sort of isomerization (or 1,3-sigmatropic rearrangement) occurs thermally in the case of an antara-surface shift of hydrogen (scheme a); a supra-surface shift (scheme b) is forbidden by symmetry [4].

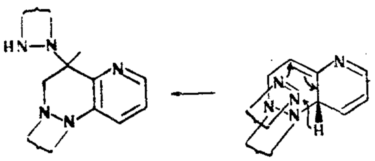


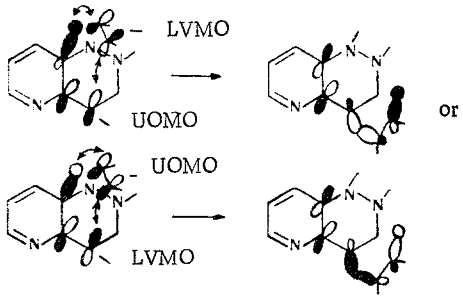
It is apparent that positive overlap between the orbital of the carbon skeleton and the orbital of the migrating hydrogen atom is retained only in the case of an antara-surface shift. This excludes the formation of high-energy orbitals, and as a result a symmetry-permitted antara-surface migration of hydrogen (scheme a) occurs.

In intermediate adduct A, because of steric hindrance, an antara-surface shift of hydrogen is difficult to realize, and this explains the impossibility of the formation of monoadduct V.

However, a different process that leads to aromatization of the pyridine ring seems real. The reaction of intermediate A with a new dienophile molecule may proceed via the mechanism of the "ene synthesis" or substitutive addition with shifting of the double bond in the pyridine ring, migration of hydrogen to the dienophile molecule, and addition of the latter to the end of the allyl system of intermediate A.

We note that an ene synthesis of this type is observed quite frequently — in the reaction of styrene with azodicarboxylic acid ester [2], the reaction of 2-vinylpyridine with N-butylmaleinimide [6], etc. — and is evidently of a general nature. The interaction of the molecular orbitals of the reacting system can be represented, in accordance with perturbation theory [5], as interaction of the upper occupied molecular orbital (UOMO) of the ene with the lower vacant molecular orbital (LVMO) of the enophile or of the UOMO of the enophile with the LVMO of the ene.





EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra of concentrated hydrochloric acid solutions of the compounds were recorded with a Pye Unicam-8000 spectrophotometer. The PMR spectra of trifluoroacetic acid solutions of the compounds were recorded with a Varian T-60 spectrometer with hexamethyldisiloxane as the external standard. The mass spectra were obtained with a Gnom MAT-111 spectrometer with introduction of the substances into the ionization region at an ionizing-electron energy of 80 eV.

4-Phenyl-1,2,4-triazoline-3,5-dione (I). This compound was obtained by the method described in [7].

2-Phenyl-1,3-dioxo-4-(4-phenyl-3,5-dioxo-1,2,4-triazolin-1-yl)triazolo[1,2-*a*]-1,2,3,4-tetrahydro-5-azacinnolines (IVa-e). All of these compounds were obtained by the following general method. A solution of 0.02 mole of I in 50 ml of absolute ether was added to a solution of 0.015 mole of freshly distilled vinylpyridine in 10 ml of absolute ether, and the mixture was allowed to stand at room temperature. After 1 h, the resulting precipitate was removed by filtration and recrystallized from chloroform.

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