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INDAZOLEQUINONES IN THE NENITZESCU REACTION. SYNTHESIS OF PYRROLO[2,3-*e*]- AND FURO[2,3-*e*]INDAZOLES

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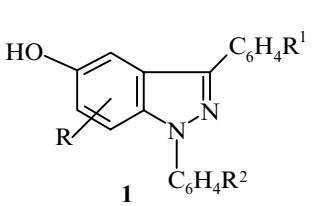
A heterocyclic quinone was used in the Nenitzescu reaction for the first time. New tricyclic compounds – pyrrolo[3,2-e]- and furo[3,2-e]indazoles – were synthesized by the condensation of 1,3-diphenyl-4,7-dioxoindazole with various enamines.

Keywords: indazolequinone, pyrroloindazole, furoindazole, Nenitzescu reaction.

Recently we discovered a new reaction, called the aza-Nenitzscu reaction, involving the reaction of benzoquinones with azaenamines – hydrazones. As a result of the reaction the derivatives of 5-hydroxyindazole **1** and indazolequinone **2** were synthesized [1, 2].



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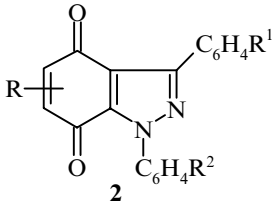

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An attractive direction in the synthetic use of indazolequinones **2** is their introduction into the Nenitzescu reaction in order to annellate the system with pyrrole and/or furan rings. Before the present work heterocyclic quinones had not been used in the Nenitzescu reaction [3-5].

The aim of the present work was to study the condensation of 1,3-diphenyl-4,7-dioxoindazole **2** ($R = R^1 = R^2 = H$) with various enamines, to investigate the reaction paths, and to determine its application limits.

It is known that the Nenitzescu reaction can take place in several directions (e.g., with the formation of 5- and 6-hydroxyindoles, 5-hydroxybenzofurans, derivatives of 4,5-dihydroxyindole, etc.) even when the simplest quinones are used [3, 4]. The use of unsymmetrical quinones, such as quinone **2**, in this reaction increases the possibility of the realization of alternative directions by many times. The determining stage of the process as a whole is the initial formation of a C–C bond between quinone and enamine; here the carbon atom at the β-position of enamine attacks the carbon atom of quinone with the highest partial positive charge preferentially. Examination of the structure of indazolequinone **2** from this standpoint leads to the conclusion that the electron-withdrawing effect of the 4-oxo group is reduced on account of conjugation with the unshared electron pair of the $N_{(1)}$ atom, and position 5 must be the main point of preferential attack by enamine.

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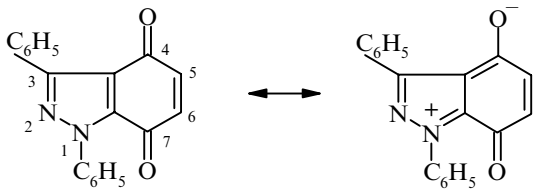
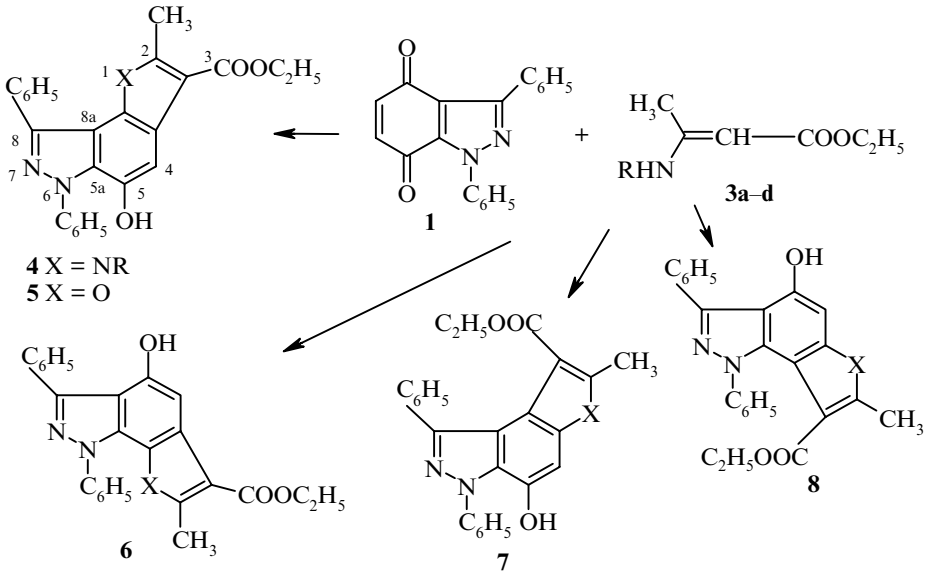


It is of course impossible to reject conclusively on the basis of the arguments alone the possibility of attack by enamine at position 6 of quinone **2** and also attack at the carbon atoms of the carbonyl groups $C_{(4)}$ or $C_{(7)}$. (In this case 6-hydroxyindoles are usually formed in the Nenitzescu reaction [3, 4, 6].) At the first stage of the investigation the derivatives of β-aminocrotonic ester **3a-d** were brought into reaction with quinone **2**. In view of the possible directions of the Nenitzescu reaction the formation of the following compounds could be expected as a result of the reactions:



4 X = NR
5 X = O

4a R = CH_3; **b** R = $C_6H_5CH_2$; **c** R = H; **d** R = *p*-$CH_3OC_6H_4$

The reaction products were identified by ^1H and ^{13}C NMR spectroscopy. It is of course extremely easy to choose between pyrroloindazoles and furoindazoles by means of the ^1H NMR spectra, since the latter do not contain the signals of the substituents at position 1 of the new ring (Table 1). To determine the direction of annellation we used the ^{13}C NMR spectra, recorded without proton decoupling, and the data from selective resonance. The NMR analysis was conducted on the products from the reaction of indazolequinone **2** with enamines **3a**,**c**,**d**. Table 2 gives the chemical shifts and spin–spin coupling constants $^2J_{C–H}$ and $^3J_{C–H}$ of the quaternary carbon atoms of the obtained compounds. According to the chemical shifts these compounds can be broken down into two groups. In the downfield region (130-143 ppm) there are the signals for the carbon atoms attached to the heteroatoms. In the upfield region (104-122 ppm) there are the signals for the carbon atoms distant from the nitrogen and/or oxygen atoms. The signals with spin–spin coupling constants in the range of 7-9 Hz were assigned to the carbon atoms located three bonds away from the proton at position 4. For furoindazoles these signals are in the range of 130-143 ppm (Table 2). In the spectra of pyrroloindazoles one of the signals is also observed in the downfield region, whereas the other is shifted upfield (119-122.5 ppm). Nevertheless this signal was assigned to the carbon atom at the α-position of the pyrrole ring. The accuracy of this assignment follows from the selective decoupling spectra. For the compound obtained from enamine (**3a**) the signal at 122.2 ppm, which has the form of a multiplet, is converted during the decoupling of 1-CH_3 (3.11 ppm) into a doublet ($^3J_{C–H}$ = 8.5 Hz). Such a downfield shift is probably due to the presence of an electron-donating hydroxy group at the *para* position. The observed arrangement of the signals, split with a large spin–spin coupling constant, makes it possible to exclude structures **7** and **8**, since in this case splitting with a large spin–spin coupling constant would be observed for the carbon atoms in the upfield region, since they are at the β-position of the furan (pyrrole) ring, i.e., at 110-112 ppm.

TABLE 1. The ^{1}H NMR Spectra of Compounds **4a-d**, **5**, **10a-c**, **11a,b**

Compound	Chemical shifts, δ, ppm					
	1-CH_3, 1-H, 1-$\underline{CH_2}C_6H_5$, 1-C_6H_4–$O\underline{CH_3}$-*p*	2-CH_3	3-$COOC_2H_5$, 3-$COCH_3$	4-H	5-OH	Aromatic protons of substituents
4a	3.11 s	2.57 s	1.36 t, 4.28 q, *J* = 7.22 Hz	7.66 s	9.79 br. s	7.35-7.64 m (10H)
4b	5.01 s	2.44 s	1.36 t, 4.29 q	7.72 s	9.84 br. s	7.0-7.6 m (13H), 6.10 m (2H)
4c	10.95 br. s	2.67 s	1.37 t, 4.29 q	7.60 s	9.65 br. s	7.36-7.66 m, 7.85 m (10H)
4d	3.67 s	2.34 s	1.36 t, 4.29 q	7.73 s	9.86 br. s	6.48 m (2H), 7.35-7.52 m (5H), 6.90-7.15 m (7H)
5		2.80 s	1.37 t, 4.29 q	7.43 s	10.22 br. s	7.40-7.68 m (8H), 8.20 m (2H)
10c	3.68 s	1.90 s		7.30 s	9.80 br. s	6.48 m (2H), 6.98-7.16 m (7H), 7.34-7.84 m (10H)
11a		2.82 s	2.58 s	7.57 s	10.17 br. s	7.40-7.68 m (8H), 8.20 m (2H)
11b		2.44 s		7.02 s	10.08 br. s	7.40-7.74 m (11H), 7.81 m (2H), 8.23 m (2H)
Mixture of **10b** and **11a**	5.0 s	2.42 s 2.83 s	2.52 s 2.59 s	7.85 s 7.58 s	9.58 br. s 10.04 br. s	6.34 m, 7.14 m, 7.26-7.66 m, 8.20 m*
Mixture of **10a** and **11a**	3.66 s	2.32 s 2.83 s	2.56 s 2.58 s	7.87 s 7.57 s	9.90 br. s 10.20 br. s	6.57 m, 6.90-7.14 m, 7.32-7.68 m, 8.20 m*[2]

* The chemical shifts of the protons for the unpurified substance, containing a mixture of compounds **10b** and **11a** in a ratio of ~14:76 are given.

*[2] The chemical shifts of the protons for the technical product, containing **10a** and **11a** in a ratio of ~30:70, are given.

It is seen from the examination of structures **4** and **5** that the choice of structure depends on the accuracy of the assignment of the signals for the carbon atoms present in coupling with the indazole ring, i.e., $C_{(5a)}$ and $C_{(8a)}$. Since the α-carbon atom of the pyrrole ring in pyrroloimidazoles is shifted upfield under the influence of the OH group at the *para* position, the need arises to be convinced that the signal of the $C_{(5a)}$ atom (compound **4**) is in the upfield region compared with the signal of $C_{(8a)}$ (compound **4**). We were not therefore restricted by the assertion that the carbon atoms attached to the heteroatoms should be in the downfield region, and we compared our data with the chemical shifts in the ^{13}C NMR spectra of indazole, 1,3-diphenylindazole, and 1,3-diphenyl-4,7-dihydroxyindazole obtained by calculation (Table 3).*

Comparison of these data with the data in Table 2 confirms the accuracy of the assignment of the signal of the $C_{(5a)}$ carbon in the investigated compound (130.3 ppm) compared with the signal of $C_{(8a)}$ (121.6 ppm). The presence of the splitting ($^3J_{C\text{-}5a,4\text{-}H}$ = 8.4 Hz) in conjunction with the other data makes it possible to state specifically that compounds with pyrrolo[2,3-*e*]indazole **4a-d** and furo[2,3-*e*]indazole **5** structures are formed as a result of the condensation of quinone **2** with enamines **3a-d**.

* The authors thank Candidate of Chemical Sciences V. A. Makarov for the computer emulation of the ^{13}C NMR spectra.

TABLE 2. The ^{13}C NMR Spectra (δ, ppm and SSCC (*J*, Hz)) of Compounds **4a**,**c**,**d**, **5**, **11a**,**b**

Com-pound	C-2	C-3	C-3a	C-5	C-5a	C-8	C-8a	C-8b	C-1'	C-1"	C-4	Substituents*[2]
4a	142.1 m	103.9 q*	112.0 s	139.1 d $^2J_{C\text{-}5,4\text{-}H}$ = = 2.3	130.3 d, $^3J_{C\text{-}5a,4\text{-}H}$ = = 7.2	143.8 t, $^3J_{C\text{-}8,H\text{-}2''}$ = = $^3J_{C\text{-}8,H\text{-}6''}$ = 4.0	121.6 s	122.2 m	141.0 t, $^3J_{C\text{-}1',H\text{-}3'}$ = = $^3J_{C\text{-}1',H\text{-}5'}$ = = 8.5	136.0 q, $^3J_{C\text{-}1'',H\text{-}3''}$ = = $^3J_{C\text{-}1'',H\text{-}5''}$ = = 7.6	104.1 d, $^1J_{CH}$ = = 161.8	12.0 (CH_3) 14.6 (CH_3), 34.9 (1-CH_3), 58.9 (CH_2), 165.2 (C=O)
4c	141.7 m, $^2J_{C\text{-}2,2\text{-}CH_3}$ = 7.0, $^2J_{C\text{-}2,1\text{-}H}$ = 2.2	104.0	110.8 s	139.2 d $^2J_{C\text{-}5,4\text{-}H}$ = = 2.2	130.1 d, $^3J_{C\text{-}5a,4\text{-}H}$ = = 7.8	143.9 t, $^3J_{C\text{-}8,H\text{-}2''}$ = = $^3J_{C\text{-}8,\ H\text{-}6''}$ = 4.6	122.5 d, $^3J_{C\text{-}8a,1\text{-}H}$ = = 6.1	119.0 q, $^3J_{C\text{-}8b,4\text{-}H}$ = 8.3, $^2J_{C\text{-}8b,1\text{-}H}$ = = 4.5	141.1 t, $^3J_{C\text{-}1',H\text{-}3'}$ = = $J_{C\text{-}1',H\text{-}5'}$ = = 8.4	133.6 t, $^3J_{C\text{-}1'',H\text{-}3''}$ = = $^3J_{C\text{-}1'',H\text{-}5''}$ = = 7.6	104.2 d, $^1J_{CH}$ = = 161.0	14.0 (CH_3), 14.6 (CH_3), 58.9 (CH_2), 165.4 (C=O)
4d	142.6 q, $^2J_{C\text{-}2,2\text{-}CH_3}$ = 6.8	105.2 q	111.1 s	139.7 c	130.8 d, $^3J_{C\text{-}5a,4\text{-}H}$ = = 7.2	144.0 t, $^3J_{C\text{-}8,H\text{-}2''}$ = = $^3J_{C\text{-}8,H\text{-}6''}$ = 3.8	122.1 s	122.5 d, $^3J_{C\text{-}8b,4\text{-}H}$ = = 7.6	141.0 t, $^3J_{C\text{-}1',H\text{-}3'}$ = = $^3J_{C\text{-}1',H\text{-}5'}$ = = 8.8	135.3 t, $^3J_{C\text{-}1'',H\text{-}3''}$ = = $^3J_{C\text{-}1'',H\text{-}5''}$ = = 7.5	103.8 d, $^1J_{CH}$ = = 162.5	13.2 (CH_3), 14.6 (CH_3), 54.9 (OCH_3), 59.2 (CH_2), 165.2 (C=O)
5	160.5 q, $^2J_{C\text{-}2,2\text{-}CH_3}$ = 7.7	108.8 q	110.0 s	141.1 d $^2J_{C\text{-}5,4\text{-}H}$ = = 3.0	130.0 d, $^3J_{C\text{-}5a,4\text{-}H}$ = = 8.4	142.9 t, $^3J_{C\text{-}8,H\text{-}2''}$ = = $^3J_{C\text{-}8,H\text{-}6''}$ = 4.6	120.0 s	138.2 d, $^3J_{C\text{-}8b,4\text{-}H}$ = = 9.2	140.7 t, $^3J_{C\text{-}1',H\text{-}3'}$ = = $^3J_{C\text{-}1',H\text{-}5'}$ = = 8.8	132.4 t, $^3J_{C\text{-}1'',H\text{-}3''}$ = = $^3J_{C\text{-}1'',H\text{-}5''}$ = = 8.4	103.0 d, $^1J_{CH}$ = = 163	14.2 (CH_3), 14.3 (CH_3), 60.0 (CH_2), 163.5 (C=O)
11a	160.0 q, $^2J_{C\text{-}2,2\text{-}CH_3}$ = 6.8	117.7 q	109.8 s	141.2 d $^2J_{C\text{-}5,4\text{-}H}$ = = 3.0	130.8 d, $^3J_{C\text{-}5a,4\text{-}H}$ = = 7.6	143.8 t, $^3J_{C\text{-}8,H\text{-}2''}$ = = $^3J_{C\text{-}8,H\text{-}6''}$ = 3.8	120.2 s	138.2 d, $^3J_{C\text{-}8b,4\text{-}H}$ = = 9.2	140.8 t, $^3J_{C\text{-}1',H\text{-}3'}$ = = $^3J_{C\text{-}1',H\text{-}5'}$ = = 8.4	132.5 t, $^3J_{C\text{-}1'',H\text{-}3''}$ = = $^3J_{C\text{-}1'',H\text{-}5''}$ = 7.6	103.4 d	15.5 (CH_3), 30.6 (CO<u>CH_3</u>), 193.7 (<u>CO</u>CH_3)
11b	159.2 q, $^2J_{C\text{-}2,2\text{-}CH_3}$ = 6.8	117.1 q	110.0 s	141.2 d $^2J_{C\text{-}5,4\text{-}H}$ = = 2.3	131.0 d, $^3J_{C\text{-}5a,4\text{-}H}$ = = 8.6	143.0 t, $^3J_{C\text{-}8,H\text{-}2''}$ = = $^3J_{C\text{-}8,H\text{-}6''}$ = 4.6	120.7 s	138.5 d, $^3J_{C\text{-}8b,4\text{-}H}$ = = 9.1	140.7 t, $^3J_{C\text{-}1',H\text{-}3'}$ = = $^3J_{C\text{-}1',H\text{-}5'}$ = = 9.0	132.4 t, $^3J_{C\text{-}1'',H\text{-}3''}$ = = $^3J_{C\text{-}1'',H\text{-}5''}$ = = 8.6	102.6 d, $^1J_{CH}$ = = 163.3	14.8 (CH_3), 191.5 (CO)

* The signal is split on account of coupling with the protons of the methyl group at C-2 and the proton at C-4 with suppression of coupling, with which it is transformed into a quartet ($^3J_{C\text{-}2,2\text{-}CH_3}$).

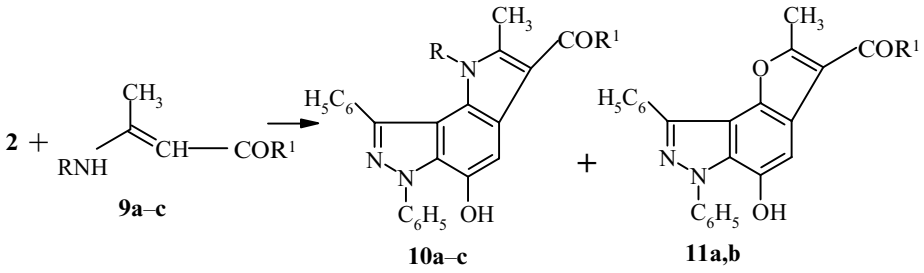
*[2] The signals of 6-C_6H_5, 8-C_6H_5, $CH_2C_6H_5$, $C_6H_4OCH_3$ are observed in the region of 126.4-130.6 and for **11b** 126.4-139.1 ppm.

TABLE 3. The ^{13}C NMR Spectra of the Derivatives of Indazole

Compound	Chemical shifts, δ, ppm						
	C-3	C-4	C-5	C-6	C-7	C-3a	C-7a
Indazole	133.4	120.4	120.1	125.8	110,0	122.8	139.9
1,3-Diphenylindazole	144.8	126.6	125.2	123.7	109.8	127.8	141.1
1,3-Diphenyl-4,7-dihydroxy-indazole	148.6	153.3	110.9	111.24	135.5	111.0	131.4

If enamines **3a-c** are used the predominant direction of the Nenitzescu reaction is the formation of pyrroloindazoles (the indole cyclization path). Thus, for enamines **3a,b** the derivatives **4a,b** are formed almost entirely (benzofuran **5** was found as minor impurity in the unpurified product obtained as a result of the reaction of quinone **2** and enamine **3a**), while the unpurified mixture of products from the reaction of enamine **3c** contains pyrrole **4c** and furan **5** derivatives in a ratio of ~92:8 (data from the ^1H NMR spectrum). On the other hand the reaction of indazolequinone **2** with N-aryleneamine **3d** leads to a mixture in which furoindazole predominates (**4d** : **5** ratio ~40:60). This mixture was separated by column chromatography, and compounds **4d** and **5** were identified.

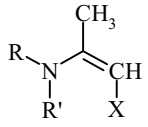
The natural continuation of the work was to study the reactions of indazolequinone **2** with enamino ketones **9a-c**. Evidence for the structure of the obtained tricycles was obtained according to the scheme described above using the ^1H and ^{13}C NMR spectra (Tables 1 and 2). It was established that, as in the case of aminocrotonic esters, the derivatives of pyrrolo- and furo[2,3-*e*]indazoles **10a-c, 11a,b**) are formed as a result of these reactions.



9a, **10a** R = *p*-$CH_3OC_6H_4$, $R^1 = CH_3$; **9b**, **10b** R = $C_6H_5CH_2$, $R^1 = CH_3$;
9c, **10c** R = *p*-$CH_3OC_6H_4$, $R^1 = C_6H_5$; **11a** R = CH_3, **11b** R = C_6H_5

The ^1H NMR spectra of the unpurified substances indicate that the use of enamino ketones leads to the preferential formation of the furan-containing tricycles; the ratios of the compounds are **10a** : **11a** ~ 30 : 70; **10b** : **11a** ~ 20 : 80; **10c** : **11b** ~ 33 : 67. The products from indole cyclization could not be isolated in the individual form, and compounds **10c** and **11b** were separated by recrystallization.

Exactly like the tertiary enamines **13** under the same conditions, where quinone **2** reacts with enamines **3a-d** and **9a-c**, attempts at the Nenitzescu reaction between quinone **2** and β-nitro- or β-cyanoenamines were unsuccessful – in all cases only the initial compounds were isolated.



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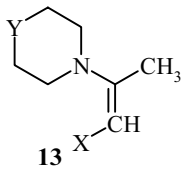
R = *i*-C_3H_7, R^1 = H, X = NO_2;
R = $R^1 = CH_3$, X = NO_2;
R = C_6H_5, R^1 = H, X = CN



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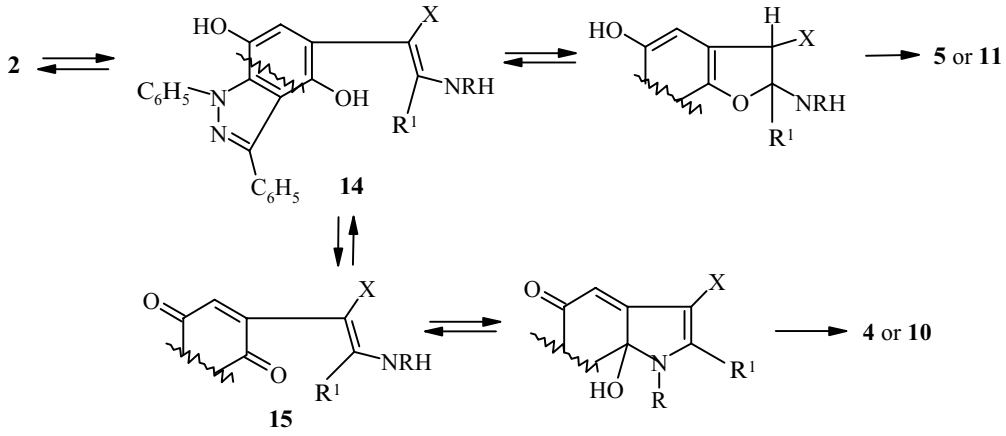
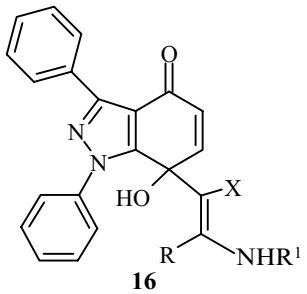
X = $COOC_2H_5$, Y = O;
X = $COCH_3$, Y = CH_2

Thus, the obtained results are related to problems that are to some degree typical during discussion of the Nenitzescu reaction, i.e., what are the reasons for the preferential occurrence of indole or benzofuran cyclization and what are the limits for the possible realization of indole or benzofuran cyclization by the Nenitzescu reaction, which are determined by the structural features of the initial enamines. In order to interpret the data on the ratio of the furo- and pyrroloindazoles it is necessary to examine the initial stages of the investigated reaction.



Thus, even without a more detailed examination (for greater detail about the mechanism of the Nenitzescu reaction, see the review [4]) it is clear that benzofurans are formed directly from the hydroquinone adducts **14** and their oxidation to the adducts **15** is necessary for the indole cyclization. Hence, for the direct cyclization **14** → **5** (or **11**) acceleration can be achieved by increasing the electron-withdrawing effect of the groups X and R, facilitating attack by the unshared electron pair of the OH group (or under suitable conditions the $R–O^-$ anion) at the enamine α position. The effect of the substituents on the oxidation rate, which determines the indole direction, acts to the same side – the less electron-donating the enamine fragment, the lower the rate of the transformation **14** → **15** and the smaller the possibility of formation of the pyrrole tricycles. The transition from the N-alkyl- to the N-aryleneamines, like substitution of the $COOC_2H_5$ group at position 3 of enamines by the stronger acceptor groups $COCH_3$ or COC_6H_5, leads to a change in the indole–benzofuran ratio in favor of the latter. Further increase in the electron-accepting strength of the substituents (nitro- and cyanoenamines) greatly reduces the rate of the initial condensation, as a result of which the reaction does not go at all. We note that nitroenamines in general are characterized by a different direction for the Nenitzescu reaction (largely typical also of cyanoenamines), associated with the formation of 6-hydroxyindoles [6]. In this case the intermediates are compounds of type **16**, which are as supposed too sterically hindered.



It is possible that steric hindrances are also the main reason for the inhibition of the Nenitzescu condensation process when tertiary enamines are used. It is also not impossible that here the stability of the intermediates **14, 15** and the ensuing intermediate compounds, formed as a result of reversible processes, is important. For the secondary enamines an important role may be played by the stabilization of these compounds due to the formation of intramolecular hydrogen bonds N–H···X.

TABLE 4. The Characteristics of the Synthesized Compounds **4a-d, 5, 10c, 11a,c**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C*	Mass, M^+	Yield, %
		C	H	N			
4a	$C_{26}H_{23}N_3O_3$	73.0 / 73.4	5.5 / 5.5	9.8 / 9.9	270-272	425	54
4b	$C_{32}H_{27}N_3O_3$			8.1 / 8.4	256-258	501	43
4c	$C_{25}H_{21}N_3O_3$			10.0 / 10.2	268-271	411	53
4d	$C_{32}H_{27}N_3O_3$	74.2 / 74.3	5.3 / 5.3	8.1 / 8.1	277-279	517	18
5	$C_{25}H_{20}N_2O_4$	73.3 / 72.8	4.9 / 4.9	6.8 / 6.8	269-271	412	11
10c	$C_{36}H_{27}N_3O_3$			8.0 / 7.7	283-286	549	18
11a	$C_{24}H_{18}N_2O_2$	75.7 / 75.4	4.7 / 4.7	7.4 / 7.3	279-281	382	45
11c	$C_{29}H_{20}N_2O_3$	78.1 / 78.4	4.8 / 4.5	6.6 / 6.3	231-233	444	44

* Compounds **4a,b** were recrystallized from dichloroethane, **4c,d, 5, 11a** from acetic acid, and **11c** from benzene.

In conclusion we note that the synthesis of the tricyclic indazoles may be not only of theoretical interest but also of practical significance as an approach to the search for new medicinal substances. Recently there appeared an investigation indicating the prospects for the study of polycyclic indazole-containing systems in the search for new antitumor compounds [7].

EXPERIMENTAL

The NMR spectra were recorded on a Varian Unity Plus 400 instrument in DMSO-d_6 with TMS as internal standard. The mass spectra were obtained on a Finnigan SSQ-710 chromato-mass spectrometer with direct injection of the sample into the ion source. Thin-layer chromatography was conducted on Silufol UV-254 plates with development in UV light. The characteristics of the synthesized compounds are given in Tables 1-4.

3-Ethoxycarbonyl-5-hydroxy-1,2-dimethyl-6,8-diphenylpyrrolo[3,2-*e*]indazole (4a). N-Methylamino-crotonic ester **3a** (2.25 g, 15 mmol) was added with stirring to a suspension of indazolequinone **2** (3.0 g, 10 mmol) in a mixture of acetic acid (100 ml) and acetic anhydride (1 ml) at 20°C. The mixture was stirred and heated at 55-60°C for 5-10 min, stirring was continued for 8 h, and the mixture was left overnight. The crystals that separated were filtered off, washed with acetic acid and with water, dried, and recrystallized from dichloroethane. Yield 2.3 g (54%) of compound **4a**.

Compounds **4b,c** were obtained similarly.

3-Ethoxycarbonyl-5-hydroxy-1-(4-methoxyphenyl)-2-methyl-6,8-diphenylpyrrolo[2,3-*e*]indazole (4d) and 3-Ethoxycarbonyl-5-hydroxy-2-methyl-6,8-diphenylfuro[2,3-*e*]indazole (5). The reaction was conducted under the conditions described for the synthesis of compounds **4a-c**. The isolated substance was dissolved in chloroform with the addition of ~0.5% of DMF and was chromatographed on a column of silica gel. The product was eluted with chloroform, and compounds **5** and **4d** were isolated from the eluate.

3-Acetyl-5-hydroxy-2-methyl-6,8-diphenylfuro[2,3-*e*]indazole (11a). The reaction was conducted under the conditions described for the synthesis of compounds **4a-c**. Quinone **2** and enamine **9a** (yield of compound **11a** 41.2%) or quinone **2** and enamine **9b** (yield of compound **11a** 44.9%) were used for the experiment.

3-Benzoyl-5-hydroxy-2-methyl-6,8-diphenylfuro[2,3-*e*]indazole (11b) and 3-Benzoyl-5-hydroxy-1-(4-methoxyphenyl)-2-methyl-6,8-diphenylpyrrolo[2,3-*e*]indazole (10c). The reaction was conducted under the conditions described for the synthesis of compounds **4a-c**. The isolated substance was boiled in acetic acid, and the suspension was filtered while hot. The precipitate was washed on the filter with acetic acid and with water and dried. Compound **10c** was obtained. The precipitate that separated from the acetic acid solution, containing a mixture of compounds **11b** and **10c**, was filtered off, and the acetic acid mother solution was diluted with water. The precipitate was filtered off, washed with water, dried, and recrystallized from benzene. Compound **11b** was obtained.

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