ISSN 1070-4280, Russian Journal of Organic Chemistry, 2018, Vol. 54, No. 8, pp. 1189–1199. © Pleiades Publishing, Ltd., 2018.
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Thermal Rearrangements of 3*H*- and 4*H*-Pyrazoles Prepared by Reactions of 9-Diazofluoren with Methyl Tetrolate and Methyl 3-Phenylpropiolate

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Received August 2, 2017

Abstract—9-Diazofluoren adds in Et_2O at 20°C to methyltetrolate in keeping with Auwers rule and non-regioselectively adds to methyl-3-phenylpropiolate with the formation of spirocyclic 3*H*-pyrazoles. The methyltetrolate adduct at boiling in toluene converts into methyl 3a-methyl-3a*H*-dibenzo[*e,g*]indazole-3-carboxylate, at 190°C in benzene, into methyl 3-methyl-2*H*-dibenzo[*e,g*]indazole-2-carboxylate, and at 160°C in methanol, into 3-methyl-2*H*-dibenzo[*e,g*]indazole. Auwers adduct of methyl 3-phenylpropiolate at boiling in benzene gives cyclopropene derivative and at boiling in methanol isomerizes into methyl 3a-phenyl-3a*H*-dibenzo[*e,g*]indazole-3-carboxylate. Anti-Auwers adduct at boiling in benzene isomerizes into methyl 2-phenylpyrazolo[1,5-*f*]phenanthridine-3-carboxylate.

DOI: 10.1134/S1070428018080122

3,3-Disubstituted 3*H*-pyrazoles and 4,4-disubstituted 4*H*-pyrazoles are compounds conformable to 5,5-disubstituted cyclopentadienes, and they may undergo typical for the latter sigmatropic rearrangements [1], consisting in 1,5-shift of substituent from a saturated carbon atom [2–4]. Considerably more examples of such transformations are known for 3*H*-pyrazoles than for 4*H*-pyrazoles [5, 6]. Yet the problem of establishing the dependence of the rearrangement direction on structural features of initial compounds and external conditions is topical and remains unsolved up till now, and since the products proper are practically interesting the research on this issue continues [7–11].

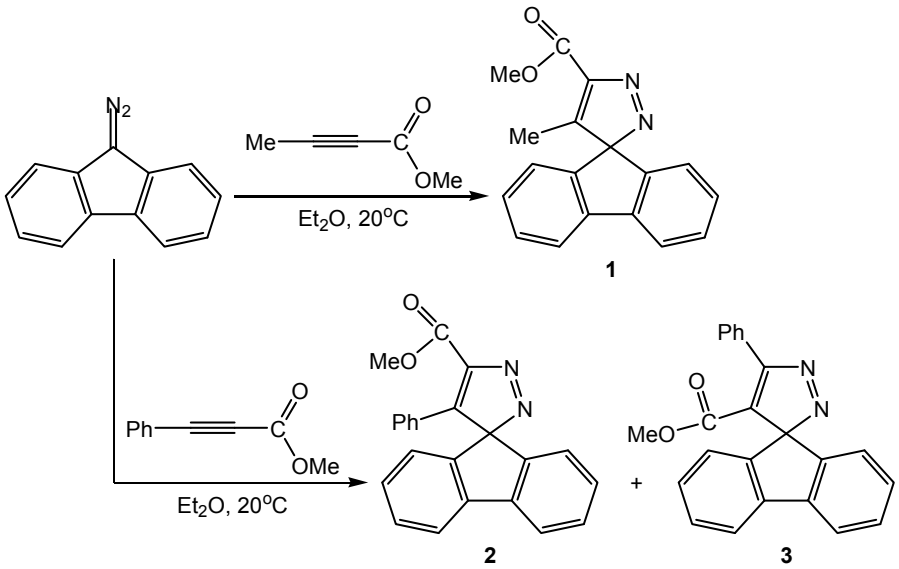
The main method of synthesis of the mentioned 3*H*-pyrazoles is the 1,3-dipolar cycloaddition of disubstituted diazomethanes to activated acetylenes, and the easiest way to 4*H*-pyrazoles is the isomerization of these 3*H*-pyrazoles. In the present study we performed reactions of cycloaddition of 9-diazofluoren to methyltetrolate and methyl 3-phenylpropiolate that allowed the preparation of attractive for investigation spirocyclic 3*H*-pyrazoles and from them disubstituted 4*H*-pyrazoles, and to study their transformations.

The reaction was performed in a closed vessel in ethyl ether at 20°C without access of light during 1–2 weeks. The reaction of methyltetrolate is characterized by strict regioselectivity and leads to the formation of cycloadduct **1** corresponding to Auwers rule, like in reactions of 9-diazofluoren with acetylene sulfones [12, 13]. In contrast, the cycloaddition to methyl 3-phenylpropiolate occurs without regioselectivity: along with Auwers adduct **2** forms its regioisomer **3**, while their ratio during the course of the reaction changes, being, according to ^{1}H NMR, 2 : 1 in the first stage and 6 : 1 by the end. This result is different from the result of [14], where the formation of unique cycloadduct **2** has been reported (Scheme 1).

A characteristic signal for the structure of 3*H*-pyrazole in ^{13}C NMR spectra of compounds **1–3** is the peak of the spirocyclic carbon atom at ~110 ppm [12, 13]. The presence of two possible regioisomers **2** and **3** allows for establishing their structure by comparing ^{1}H NMR spectra. Luckily the points of comparison,

† Deceased.

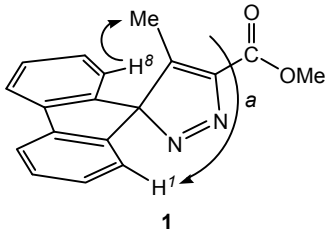
Scheme 1.



chemical shifts of *ortho*-protons of phenyl ring and protons of methoxycarbonyl group, are different in the spectra of regioisomers, and these differences on qualitative level may be connected with the structural diversity. So, the most downfield signal (δ 8.35 ppm) corresponds to the *ortho*-protons of phenyl group in isomer **3**, because of the deshielding effect of the adjacent CO_2Me group and the azo-fragment. In isomer **2** the corresponding signal is considerably shifted upfield (δ 7.04 ppm). At the same time in isomer **2** the chemical shift of group CO_2Me (δ 4.07 ppm), suffering deshielding effect of the N=N fragment, exceeds chemical shift of the same group in isomer **3** by 0.64 ppm.

To confirm the structure of 3*H*-pyrazol **1** we have registered the ^1H–^1H NOESY spectrum looking for the cross-peak *a* corresponding to the interaction of spatially close protons of methyl group and protons $H^{1,8}$ of fluorenyl residue that was impossible for anti-Auwers regioisomer of this compound. According to the structure of compound **1** the signal of protons of CO_2Me group is present in the ^1H spectrum in the same position as in the spectrum of compound **2** (Scheme 2).

Scheme 2.

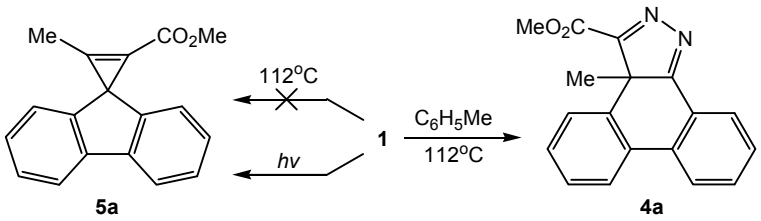


Hence, we got three 3*H*-pyrazoles, two of which, compounds **1** and **2**, belong to derivatives with an acceptor substituent in the position *5*, and 3*H*-pyrazol **3**, to a derivative with an acceptor substituent in the position *4*.

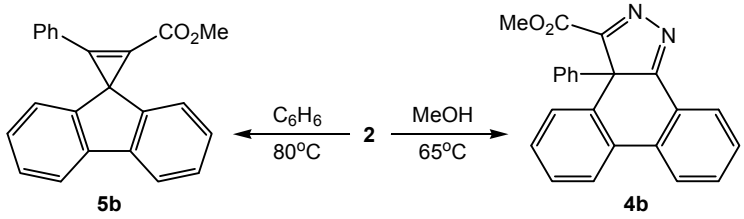
We established that 3*H*-pyrazole **1** at boiling in toluene (112°C, 2 h) gives a single product: a derivative of 4*H*-pyrazole indazole **4a**. It is known that some 3*H*-pyrazoles at thermolysis may undergo fragmentation with the formation of cyclopropene derivatives [12, 15–17]. In the case in question it did not happen, and this conclusion was reliably confirmed, when the anticipated spirocyclic cyclopropene **5a** was specially synthesized by UV irradiation of 3*H*-pyrazole **1** in a quartz test tube in CH_2Cl_2 (20°C, 4 h), cf. [12] (Scheme 3).

In favor of the structure assigned to 4*H*-pyrazole **4a** evidences the presence in the ^{13}C NMR spectrum of two signals of carbon atoms of dimethylenehydrazine fragment in a weak field at δ ~176 and 183 ppm and two signals in a strong field at 28.7 (Me) and 65.9 ppm (quaternary carbon atom), cf. [13]. Moreover, in the UV spectrum of this compound a characteristic absorption band at 311 nm (log ε 3.96) is detected, cf. [6]. For cyclopropene **5a** a strong absorption band is characteristic in the IR spectrum at 1863 cm^{-1} of stretching vibrations of the multiple bond C=C comparable by intensity with the absorption band of the conjugated to it carbonyl group [18, 19]. Besides that in ^{13}C NMR spectrum the signal of spirocyclic carbon atom present at ~41 ppm is characteristic [12].

Scheme 3.

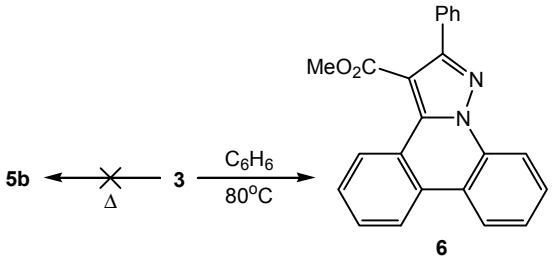


Scheme 4.



3*H*-Pyrazole **2** turned out to be much less stable thermally compared to its methyl-substituted analog **1**. At boiling in benzene during 8 h a full conversion was achieved, and no rearrangement took place, only the fragmentation affording cyclopropene derivative **5b**. Boiling of pyrazole **2** in methanol results in a rearrangement, similar to that observed for analog **1**, namely, a single product was obtained, 4*H*-pyrazole **4b** (Scheme 4). Such result correlates with conclusions of [17] on the significantly increasing contribution of a competitive reaction of denitrogenation at the thermolysis of 3*H*-pyrazoles in aprotic solvent (benzene) compared to their thermolysis in polar solvent (acetonitrile, methanol, ethanol).

Scheme 5.



The structure of 4*H*-pyrazole **4b** is recognized by downfield signals in the ^{13}C NMR spectra at 168.7 and 182.7 ppm of dimethylenehydrazine fragment and by characteristic absorption in UV spectra at 300 (log ε

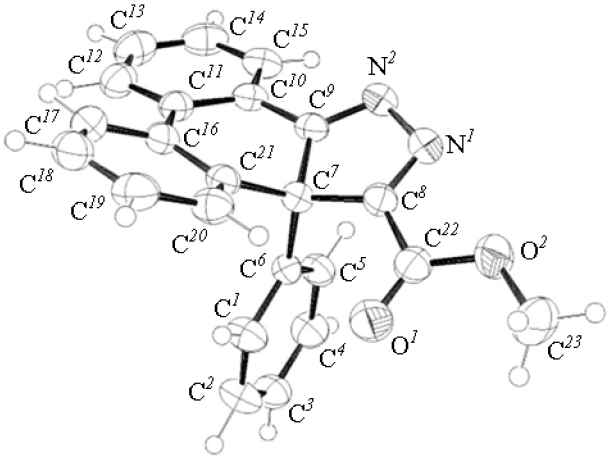


Fig. 1. Spatial arrangement of methyl 3a-phenyl-3a*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **4b** molecule in the crystal by XRD data.

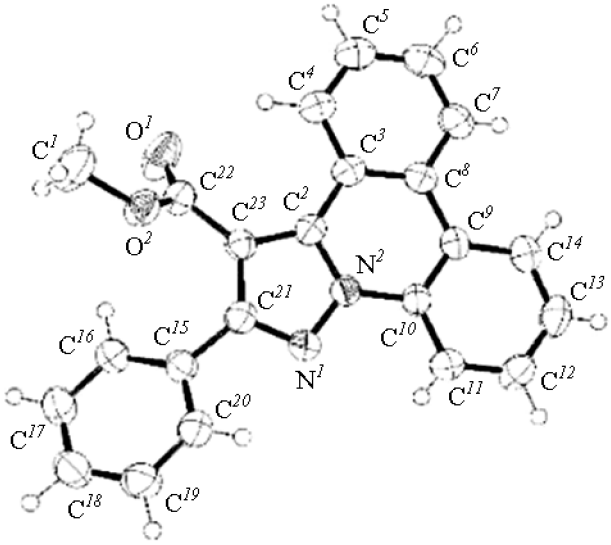
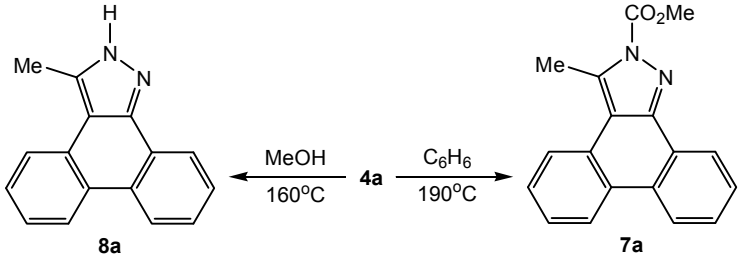
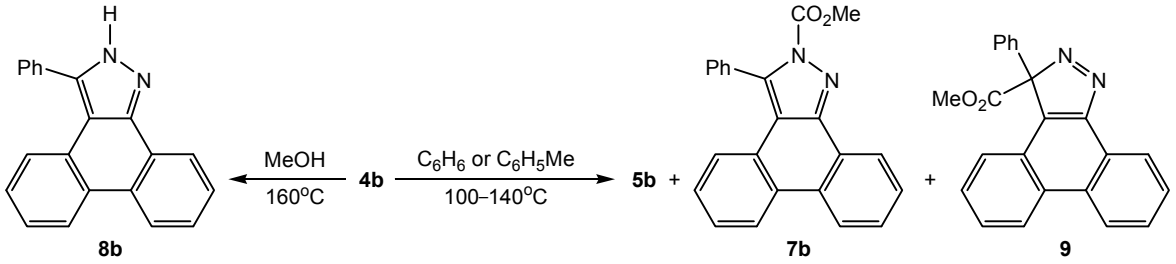


Fig. 2. Spatial arrangement of the methyl 2-phenylpyrazolo-[1,5-*f*]phenanthridine-3-carboxylate **6** molecule according to XRD analysis.

Scheme 6.



Scheme 7.



3.95) and 308 (log ε 3.68) nm (see above). A strict confirmation of the structure of 4*H*-pyrazole **4b** was obtained by X-ray diffraction (XRD) analysis of its single crystal (see the table, Fig. 1).

Cyclopropene **5b** was identified by the absorption band in IR spectrum at 1836 cm^{-1} and the characteristic signal of quaternary carbon atom at ~40.5 ppm in the ^{13}C NMR spectrum (see above).

Spirocyclic 3*H*-pyrazole **3** at boiling in benzene during 12 h fully transformed into 1*H*-pyrazole **6** (Scheme 5). Yet the fragmentation of compound **3** and the formation of cyclopropene **5b** did not occur.

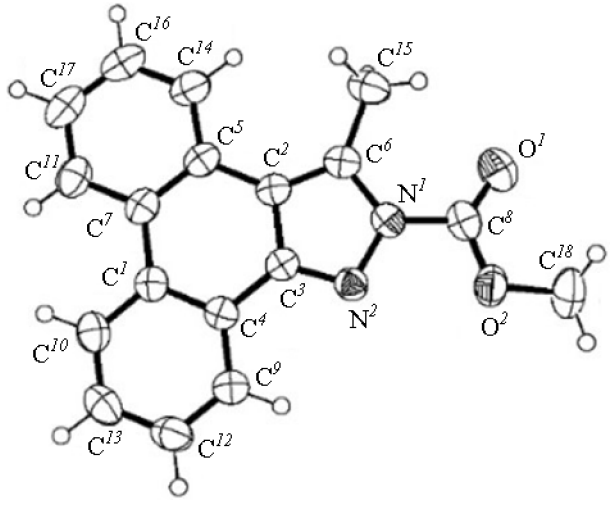


Fig. 3. Spatial arrangement of the methyl 3-methyl-2*H*-dibenzo[*e*,*g*]indazole-2-carboxylate **7a** molecule according to XRD analysis.

The structure of compound **6** is confirmed by IR, ^1H and ^{13}C NMR spectra and the data of XRD analysis of its single crystals (see the table, Fig. 2).

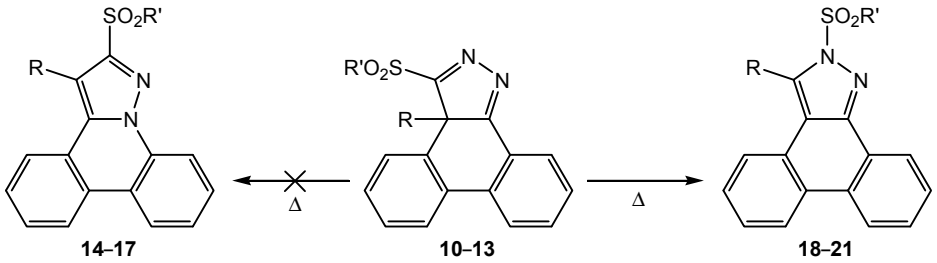
Further we investigated thermal transformations of two 4*H*-pyrazoles **4a** and **4b** that we obtained. Compound **4a** at high temperature (microwave reactor, benzene, 190C, 40 min) isomerized into indazole **7a**, and at 160°C in methanol fragmentized with the formation of *N*-unsubstituted 1*H*-pyrazole **8a** (Scheme 6).

For the confirmation of the structure of indazole **7a** we applied a correlation HMBC spectrum, which revealed the coupling of methyl group protons with the atom ^{15}N through three bonds. As a spectral feature of compound **7a** an unusually downfield chemical shift of these protons in the ^1H NMR spectrum (δ 3.19 ppm) should be mentioned. The structure of indazole **7a** was proved also by XRD analysis of its single crystal (see the table, Fig. 3).

The structure of 3-methylindazole **8a** satisfactorily correlates with ^1H and ^{13}C NMR spectra. For the assignment of signals DEPT technique was applied.

4*H*-Pyrazole **4b** at boiling in benzene (80°C) during 12 h partially (conversion 50%) converts into new 3*H*-pyrazole **9**. In the microwave reactor at 100°C after 1 h the conversion was 70%. Heating in benzene at 130°C for 20 min resulted in a full conversion and gave equal amounts of compounds **7b** and **9**. Heating of compound **4b** in toluene at 135°C during 2.5 h ends in the formation of a three-component mixture consisting of compounds **7b**, **9**,

Scheme 8.



R = Ph (**10–12**, **14–16**, **18–20**), Me (**13**, **17**, **21**); R' = Me (**10**, **14**, **18**), Ph (**11**, **13**, **15**, **17**, **19**, **21**), 4-MeC_6H_4 (**12**, **16**, **20**).

and cyclopropene **5b** in a ratio 3 : 3 : 2 (Scheme 7). Compound **5b** was identified in reaction mixture by ^{1}H and ^{13}C NMR spectra of an authentic sample. Indazole **7b** was isolated in crystalline form by flash-chromatography on silica gel. 3*H*-Pyrazole **9** was also obtained at keeping 3*H*-pyrazole **2** during 6 h in glacial acetic acid at 20°C with a catalytic quantity of conc. H_2SO_4 and it was isolated in an individual state. Heating of 3*H*-pyrazole **2** or 4*H*-pyrazole **4b** in methanol at 160°C during 20 min resulted in known indazole **8b** [12], analog of compound **8a**.

To establishing the structure of indazoles **7b** and **9** IR, ^{1}H and ^{13}C NMR spectra were applied. The chemical proof of the structure of indazole **7b**, whose ^{13}C NMR spectrum is very close to the spectrum of indazole **7a**, is its conversion into indazole **8b** at hydrolysis with air moisture at storage. Mild hydrolysis as well as methanolysis (heating in methanol at 160°C) of compounds **7a** and **7b**, occurs comparatively easily due to their being practically urethanes, and the formed aromatic 1*H*-pyrazoles **8a** and **8b** operate therewith in these processes as good leaving groups in the nucleophilic substitution at the carbonyl carbon atom.

Compound **9** is relatively unstable and at storage also transforms into indazole **8b**. The signal of the quaternary carbon atom of 3*H*-pyrazole **9** appears in the ^{13}C NMR spectrum at ~105 ppm, and of carbonyl group, at 167 ppm, close to the chemical shifts of the same groups of a model indazole, distinguished from compound **9** by the presence of one more methoxycarbonyl substituent instead of the phenyl group [17].

At the analysis of ^{13}C NMR spectra of *N*-methoxycarbonyl-substituted indazoles **7a** and **7b** we discovered their significant similarity to the spectra of products of high-temperature thermolysis of 3-sulfonyl-substituted 4*H*-pyrazoles **10–13** [12, 13]. Moreover, the heating of 4*H*-pyrazole **13** in methanol at 160°C resulted in the same indazole **8a**, which was obtained from compound **7a** in the same conditions (see above).

The latter fact calls into question the correctness of the structure determination of thermolysis products of 4*H*-pyrazoles **10–13**, which previously were attributed to phenanthridine structures **14–17** basing on XRD analysis on single crystals of thermolysis products of pyrazole **10**. We performed a repeated solution of the XRD data massive of this sample and found that it really possesses the structure of *N*-sulfonyl-substituted indazole **18** (see the table, Fig. 4).

These facts make it possible to conclude that sulfonyl-substituted 4*H*-pyrazoles **10–13** at high temperature behave similar to methoxycarbonyl-substituted 4*H*-pyrazoles **1** and **2** and are converted respectively into indazoles **18–21**, not into phenanthridines **14–17** [12, 13] (Scheme 8).

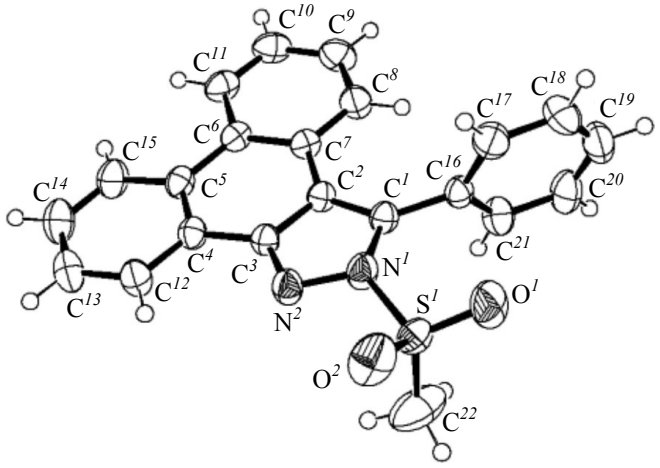
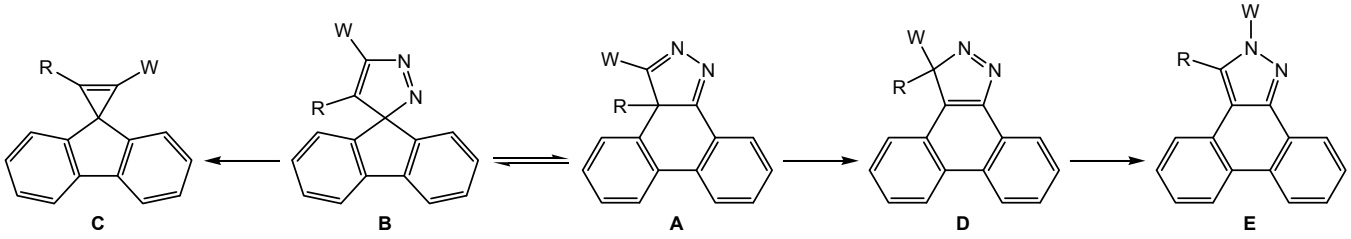


Fig. 4. Spatial arrangement of the 2-(methylsulfonyl)-3-phenyl-2*H*-dibenzo[*e,g*]indazole **18** molecule in the crystal according to XRD analysis data.

Scheme 9.



Hence the previously unexplained formation of 1*H*-pyrazole **8b** at maintaining pyrazoles **14–16** in glacial acetic acid with catalytic amount of conc. H_2SO_4 [12] becomes understandable: indeed, the hydrolysis of *N*-sulfonyl-substituted 1*H*-pyrazoles **18–20** occurs at diluting reaction mixtures with water when isolating the reaction products.

Now we can make some conclusions resulting from our investigation. Firstly, they regard the conclusions from the study of thermolysis of 3*H*-pyrazoles **1–3** derivatives. The rearrangement of these pyrazoles occurred fully in keeping with the previously discovered laws [20] and obeyed the directing effect of the acceptor substituent CO_2Me in the position *5* (of compound **1** and **2**) or *4* (of compound **3**). A significant increase in the rearrangement rate of phenyl -substituted pyrazole **2** was found compared to its methyl analog **1**. Evidently, in the bipolar intermediate state of sigmatropic shift to a carbon atom [20] the stabilizing effect of phenyl group exceeds the effect of methyl group. At the thermolysis in aprotic solvent pyrazole **2** unlike pyrazole **1** undergoes a denitrogention, not a rearrangement. Evidently, the process of fragmentation starts with the rupture of the bond between the spirocyclic carbon atom and the nitrogen atom, and further cyclopropene **5b** forms with the participation of vinylcarbene derivative, whose stability is increased due to the phenyl group.

The results of the thermolysis investigation of 4*H*-pyrazoles **4a** and **4b** show their higher thermal stability compared to their isomeric 3*H*-pyrazoles **1** and **2**. The same behavior features of 3*H*- and 4*H*-pyrazoles were observed in the series on sulfones we investigated [12, 13]. While comparing the structure of thermolysis products of related 4*H*-pyrazoles **4a**, **4b**, and **10–13**, differing only in substituents in the positions *3* or/and *4*, the high sensitivity should be mentioned of the paths of thermal transformations of these pyrazoles to the substituents nature. Indeed, the thermolysis of 4*H*-pyrazoles **4a** and **10–13** results in a single rearrangement product, *N*-acceptor-substituted 1*H*-pyrazole **E**, and its precursor, a new 3*H*-pyrazole **D** remains unobservable in the higher temperature conditions. And only from 4*H*-pyrazole **4b** along with two rearrangement products, a new 3*H*-pyrazole **D** and 1*H*-pyrazole **E**, and also a fragmentation product was obtained, derivative of cyclopropene formed via thermally unstable 3*H*-pyrazole **B** (Scheme 9).

Hence we experimentally demonstrated that for 4*H*-pyrazole **4b** at the temperature, exceeding that at which it is obtained from 3*H*-pyrazole, a possibility exists of rearrangement either to the reverse side, or to the new 3*H*-pyrazole **D**. Presumably such possibility is due to the presence of the phenyl substituent: high mobility of phenyl (comparing to methyl) group assists the formation of the new 3*H*-pyrazole **D**. On the other hand, the stabilizing effect of phenyl substituent in Auwers 3*H*-pyrazole **B** reduces the barrier of transition in this direction, and the propensity of pyrazole **B** to suffer denitrogenation results in cyclopropene **C**. Although sulfones **10–12** also contain a phenyl substituent, at the thermolysis they do not afford the new 3*H*-pyrazole **D**, because it appears to be thermally unstable due to a higher, compared to methoxycarbonyl group, mobility of sulfonyl group in 1,5-sigmatropic rearrangement [21], leading to the formation of pyrazole **E**. Less understandable is the lack of transformation of sulfones **10–12** in the direction of pyrazole **B** and further to cyclopropene **C**. Perhaps, the corresponding 3*H*-pyrazole **B** forms, but it is less prone to denitrogenation and less stable than the ester analog due to a lower π-acceptor activity of sulfonyl group and therefore a shift of equilibrium of reversible reaction occurs in favor of terminal product **E**. In case of 4*H*-pyrazole **4a** due to the lower mobility of methyl group the formation of 3*H*-pyrazole **D** requires a higher temperature, and it brings further its quick isomerization into pyrazole **E** due to the migration of CO_2Me group. The path in direction of 3*H*-pyrazole **B** is here less feasible than in the case of

Crystallographic characteristics, parameters of XRD experiment and of refinement of structures of compounds **4b**, **5a**, **7a**, and **18**

Parameter	**4b**	**5a**	**7a**	**18**
Empirical formula	$C_{23}H_{16}N_2O_2$	$C_{18}H_{14}N_2O_2$	$C_{23}H_{16}N_2O_2$	$C_{22}H_{16}N_2O_2S$
M	352.38	290.31	352.38	372.43
T, K	297(2)	297(2)	297(2)	297(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P_1^-	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/c$
Z	2	4	4	4
a, Å	8.5710(6)	7.9431(3)	13.1429(5)	9.2729(2)
b, Å	8.9793(10)	20.4568(5)	7.0343(3)	21.0531(3)
c, Å	12.5804(11)	9.235793)	19.6302(9)	9.476392)
α, deg	93.285(8)	90	90	90
β, deg	105.762(7)	111.383(4)	104.766(4)	102.771(2)
γ, deg	110.957(8)	90	90	90
V, Å^3	857.21(14)	1397.42(9)	1754.90(13)	1804.23 (6)
ρ, g/cm^3	1.365	1.380	1.334	1.371
μ, mm^{-1}	0.088	0.092	0.086	0.199
Accounting for extinction	0.24128, 1.0	Multi-scan method [27]	Multi-scan method [27], 0.811, 1.000	Multi-scan method [27]
F(000)	368	608	736	776
Crystal size, mm	0.21 × 0.14 × 0.12	0.23 × 0.138 × 0.115	0.2 × 0.15 × 0.1	0.509 × 0.452 × 0.379
Diffractometer	XtaLAB Pro: Kappa single			Gemini S, Sapphire3
Radiation	MoK_α, λ 0.71073 Å			MoK_α, λ 0.71073Å (graphite monochromator)
Scanning type	ω -scans			ω-scans
Range of data collection with respect to θ, deg	3.416–26.371	3.399–28.281	3.373–31.207	3.615–30.504
Reflections intervals	–10≤*h*=10 –11=*k*=10 –15=*l*=15	–10≤*h*=10 –27≤*k*=27 –12≤*l*=12	–18≤*h*=19 –10=*k*=9 –28=*l*=28	–13≤*h*=13 –30≤*k*=30 –13≤*l*=13
Measured reflections	7310	22822	53548	35646
Independent reflections	3296	3458	5223	5500
with $I > 2\sigma(I)$	2651	2676	3261	4852
R_{int}	0.0266	0.0365	0.0621	0.0206
Number of refined parameters	308	255	304	244
GOOF	1.095	1.07	1.023	1.127
R-factors with respect to $F^2>2\sigma(F^2)$	R_1 0.0423, wR_2 0.1228	R_1 0.0532, wR_2 0.1253	R_1 0.063, wR_2 0.15	R_1 0.0516, wR_2 0.1317
R-factors for all reflections	R_1 0.0535, wR_2 0.1289	R_1 0.0718, wR_1 0.1358	R_1 0.1117, wR_2 0.167	R_1 0.0585, wR_2 0.1367
Residual electron density, e/A^3	–0.18/0.176	–0.183/0.205	–0.188/0.334	–0.31/0.363
$(\Delta/\sigma)_{max}/(\Delta/\sigma)_{min}$	0.027/0.002	0.005/0.000	0.000/0.000	0.001/0
Software	SHELX2014 [25], WINGX [26], CrysAlisPro [27]			

phenyl analog **4b**, also due to the stability of this pyrazole to denitrogention.

We plan further to perform special investigation of post-rearrangements of 4*H*-pyrazoles of related structure.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a spectrometer JNM-ECX400 Jeol (400.1 and 100.6 MHz respectively) from solutions of compounds in $CDCl_3$. As internal refetence at measurements of chemical shifts signals were used of residual protons (δ_H 7.26) and carbon atoms (δ_C 77.16) of deuterated solvent. IR spectra were recorded on a Fourier spectrophotometer InfraLUM FT-02 from pellets with KBr. UV spectra were recorded on a two-beam UV-VID spectrophotometer UV-2600 (Shimadzu) in methanol. Elemental analysis was performed on a CHNS-analyzer vario MICRO. Analytic TLC was performed on Sorbfil plates, eluent light petroleum ether–acetone, 4 : 1, development in iodine vapor. For column chromatography silica gel Merck 60 (0.040–0.063 mm) was applied, eluent light petroleum ether–acetone, 7–3 : 1.

Methyltetrolate [22], methyl 3-phenylpropiolate [23], and 9-diazofluoren [24] were obtained by known methods.

Reaction of methyltetrolate and methyl 3-phenylpropiolate with 9-diazofluoren. General method. To a solution of 0.5 g (2.6 mmol) of 9-diazofluoren in 15 mL of anhydrous ethyl ether was added 2.3 mmol of activated acetylene in 10 mL of the same solvent. The mixture was kept at 20°C in a tightly closed flask in darkness for 2 weeks with methyltetrolate and 7 days with methyl phenylpropiolate. We obtained a derivative 3*H*-pyrazole **1** or a mixture of regioisomers **2** and **3** (2 : 1 after 1 day, 6 : 1 after 7 days) respectively. Precipitated crystals of cycloadducts **1** and **2** were filtered off and purified by crystallization. Cycloadduct **3** was isolated by column chromatography on silica gel from the mother liquor which remained after separation of crystals of compound **2**.

Methyl 4'-methylspiro[fluoren-9,3'-pyrazole]-5'-carboxylate (1). Yield 70%, mp 147–148°C (ethyl ether) IR spectrum, ν, cm^{-1}: 1732 vs (C=O), 1447 m, 1339 s, 1219 m, 1181 m, 1111 m, 1084 m, 748 s, 729 m. ^{1}H NMR spectrum, δ, ppm: 1.93 s (3H, Me), 4.06 s (3H, OMe), 6.67 d (2H, H_{arom}, *J* 7.7 Hz), 7.24 t (2H, H_{arom}, *J* 7.6 Hz), 7.46 t (2H, H_{arom}, *J* 7.7 Hz), 7.81 d (2H, H_{arom}, *J* 7.6 Hz). ^{13}C NMR spectrum, δ, ppm: 10.7 (Me), 52.5 (OMe), 110.0 ($C^{3'}$), 121.2 ($2C_{arom}$), 123.5 ($2C_{arom}$), 128.5 ($2C_{arom}$), 130.3 ($2C_{arom}$), 135.2 ($2C_{arom}$), 143.7 ($2C_{arom}$), 145.8 ($C^{5'}$), 162.0 ($C^{4'}$), 164.1 (C=O). Found, %: C 74.38; H 4.77; N 9.61. $C_{18}H_{14}N_2O_2$. Calculated, %: C 74.47; H 4.86; N 9.65.

Methyl 4'-phenylspiro[fluoren-9,3'-pyrazole]-5'-carboxylate (2). Yield 82%. Light-yellow crystals, mp 143–144°C (ethyl ether) (141°C [14]). IR spectrum, ν, cm^{-1}: 1701 vs (C=O), 1442 m, 1337 m, 1222 m, 1126 m, 756 s, 648 m. ^{1}H NMR spectrum, δ, ppm: 4.07 s (3H, OMe), 6.88 d (2H, H_{arom}, *J* 7.7 Hz), 7.01 d (2H, H_{arom}, *J* 7.5 Hz), 7.09 t (2H, H_{arom}, *J* 7.7 Hz), 7.17–7.27 m (3H, H_{arom}), 7.44 t (2H, H_{arom}, *J* 7.7 Hz), 7.81 d (2H, H_{arom}, *J* 7.5 Hz). ^{13}C NMR spectrum, δ, ppm: 52.8 (OMe), 110.2 ($C^{3'}$), 121.3 ($2C_{arom}$), 123.9 ($2C_{arom}$), 128.2 ($2C_{arom}$), 128.5 ($2C_{arom}$), 128.6 ($2C_{arom}$), 128.7 w ($C^{5'}$), 130.2 ($2C_{arom}$), 130.6 ($2C_{arom}$), 135.2 ($2C_{arom}$), 143.6 ($2C_{arom}$), 144.7 (C_{arom}), 159.6 ($C^{4'}$), 162.1 (C=O). Found, %: C 78.28; H 4.47; N 8.06. $C_{23}H_{16}N_2O_2$. Calculated, %: C 78.39; H 4.58; N 7.95.

Methyl 5'-phenylspiro[fluoren-9,3'-pyrazole]-4'-carboxylate (3). Yield 12%. Light-yellow crystals, mp 144–145°C (petroleum ether–ethyl acetate, 8 : 1). IR spectrum, ν, cm^{-1}: 1725 vs (C=O), 1620 m, 1492 m, 1435 m, 1335 s, 1207 s, 1138 m, 1092 m, 925 m, 752 s, 690 m. ^{1}H NMR spectrum, δ, ppm: 3.43 s (3H, OMe), 6.86 d (2H, H_{arom}, *J* 7.7 Hz), 7.27 t (2H, H_{arom}, *J* 7.3 Hz), 7.48 t (2H, H_{arom}, *J* 7.8 Hz), 7.57–7.62 m (3H, H_{arom}), 7.86 d (2H, H_{arom}, *J* 7.5 Hz), 8.34–8.36 m (2H, H_{arom}). ^{13}C NMR spectrum, δ, ppm: 52.3 (OMe), 110.7 ($C^{3'}$), 121.1 ($2C_{arom}$), 123.3 ($2C_{arom}$), 128.2 ($2C_{arom}$), 128.7 ($2C_{arom}$), 129.6 w ($C^{5'}$), 129.9 ($2C_{arom}$), 130.4 ($2C_{arom}$), 131.1 ($2C_{arom}$), 132.9 w (C_{arom}), 135.6 ($2C_{arom}$), 143.5 ($2C_{arom}$), 159.8 ($C^{4'}$), 162.8 (C=O). Found, %: C 78.42; H 4.67; N 8.01. $C_{23}H_{16}N_2O^2$. Calculated, %: C 78.39; H 4.58; N 7.95.

Methyl 3a-methyl-3a*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (4a). A solution of 0.1 g (34 mmol) of 3*H*-pyrazole **1** in 3 mL of anhydrous toluene was boiled for 2 h till initial compound disappeared according to TLC. Yield 96 mg (96%), mp 116–117°C (methanol). UV spectrum (methanol): λ_{max} 311 nm (log ε 3.96). IR spectrum, ν, cm^{-1}: 1709 vs (C=O), 1551 m, 1455 s, 1362 s, 1342 s, 1250 s, 1200 s, 1076 s, 1053 m, 756 vs, 729 s. ^{1}H NMR spectrum, δ, ppm: 1.67 s (3H, Me), 4.09 s (3H, OMe), 7.27 t (1H, H_{arom}, *J* 7.7 Hz), 7.35 t (1H, H_{arom}, *J* 7.5 Hz), 7.46 t (1H, H_{arom}, *J* 7.5 Hz), 7.46 t (1H, H_{arom}, *J* 7.7 Hz), 7.78 d (1H, H_{arom}, *J* 7.7 Hz), 7.85 d (1H, H_{arom}, *J* 7.7 Hz), 7.95 d (1H, H_{arom}, *J* 8.0 Hz), 8.07 d (1H, H_{arom}, *J* 7.5 Hz). ^{13}C NMR spectrum, δ, ppm: 28.7 (Me), 52.5 (OMe), 65.9 (C^{3a}), 124.2 (C_{arom}), 124.9 w (C_{arom}), 126.2 (C_{arom}), 126.6 (C_{arom}), 126.8 (C_{arom}),

128.5 (C_{arom}), 128.9 (C_{arom}), 129.0 (C_{arom}), 131.0 w (C_{arom}), 133.3 (C_{arom}), 133.7 w (C_{arom}), 136.1 (C_{arom}), 162.7 (C=O), 167.6 (C^{2a}), 182.7 (C^{3}). Found, %: C 74.60; H 4.77; N 9.59. $C_{18}H_{14}N_2O_2$. Calculated, %: C 74.47; H 4.86; N 9.65.

Methyl 3-methylspiro(cycloprop[2]en-1,9'-fluoren)-2-carboxylate (5a). In a tightly closed quartz test tube a solution of 0.2 g (0.66 mmol) of 3*H*-pyrazole **1** in 7 mL of anhydrous CH_2Cl_2 was irradiated by the light of a mercury lamp of moderate pressure DRT-400. After evaporation of solvent the oily residue was subjected to flash-chromatography on silica gel to isolate 58 mg (32%) of colorless crystals of compound **5a**, mp 119–120°C. IR spectrum, ν, cm^{-1}: 1863 m (C=C_{olefin}), 1708 vs (C=O), 1431 m, 1246 m, 1126 w, 1103 m, 1072 w, 1030 w, 802 m, 741 m, 652 w. ^{1}H NMR spectrum, δ, ppm: 2.41 s (3H, Me), 3.75 s (3H, OMe), 7.17 d (2H, H_{arom}, *J* 7.5 Hz), 7.32 t (2H, H_{arom}, *J* 7.4 Hz), 7.41 t (2H, H_{arom}, *J* 7.4 Hz), 7.87 d (2H, H_{arom}, *J* 7.6 Hz). ^{13}C NMR spectrum, δ, ppm: 10.4 (Me), 40.8 (C^{3}), 52.4 (OMe), 106.0 (C^{2}), 120.2 (2C_{arom}), 120.8 (2C_{arom}), 126.77 (2C_{arom}), 126.92 (2C_{arom}), 133.6 (C^{1}), 140.3 (2C_{arom}), 146.4 (2C_{arom}), 160.0 (C=O). Found, %: C 82.49; H 5.44. $C_{18}H_{14}O_2$. Calculated, %: C 82.42; H 5.38.

Methyl 3a-phenyl-3a*H*-dibenzo[*e,g*]indazole-3-carboxylate (4b). A solution of 5.6 mmol of 3*H*-pyrazole **2** in 4 mL of anhydrous methanol was boiled for 4 h (TLC monitoring). Yield 1.39 g (73%), yellow crystals, mp 139–140°C (methanol). UV spectrum (methanol): λ_{max} 300 nm (log ε 3.95). IR spectrum, cm^{-1}: 1728 vs (C=O), 1559 w, 1447 m, 1343 m, 1223 m, 1103 m, 1014 m, 810 w, 760 m, 729 m, 617 w, 428 w. ^{1}H NMR spectrum, δ, ppm: 3.94 s (3H, OMe), 6.70–6.74 m (2H, H_{arom}), 7.11–7.15 (3H, H_{arom}), 7.34 t (1H, H_{arom}, *J* 7.5 Hz), 7.40 t (1H, H_{arom}, *J* 7.7 Hz), 7.49 t (2H, H_{arom}, *J* 7.7 Hz), 7.81 d (1H, H_{arom}, *J* 8.1 Hz), 7.88 d (1H, H_{arom}, *J* 7.8 Hz), 7.94 t (2H, H_{arom}, *J* 7.7 Hz). ^{13}C NMR spectrum, δ, ppm: 53.3 (OMe), 74.2 (C^{3a}), 124.1 (C_{arom}), 125.7 (C_{arom}), 126.2 (2C_{arom}), 126.5 (C_{arom}), 126.8 (C_{arom}), 128.3 (C_{arom}), 128.9 (C_{arom}), 129.0 (C_{arom}), 129.2 (2C_{arom}), 129.4 (C_{arom}), 129.6 (C_{arom}), 130.5 w (C_{arom}), 133.1 (C_{arom}), 133.2 w (C_{arom}), 133.4 w (C_{arom}), 136.2 (C_{arom}), 161.8 (C=O), 168.7 (C^{2a}), 182.7 (C^{3}). Found, %: C 78.58; H 4.49; N 7.91. $C_{23}H_{16}N_2O_2$. Calculated, %: C 78.39; H 4.58; N 7.95.

Thermolysis of 3*H*-pyrazoles 2, 3 in benzene. General method. A solution of 4.2 mmol of 3*H*-pyrazole **2** or **3** in 3 mL of anhydrous benzene was boiled for 8 h. The reaction progress was monitored by TLC by disappearance of initial compound. Cyclopropene **5b** and 1*H*-pyrazole **6** were obtained.

Methyl 3-phenylspiro(cycloprop[2]en-1,9'-fluoren)-2-carboxylate (5b). Yield 95 mg (70%), colorless crystals, mp 173–174°C (methanol). IR spectrum, ν, cm^{-1}: 1836 s (C=C), 1709 vs (C=O), 1489 s, 1447 m, 1431 m, 1300 m, 1285 m, 1204 s, 1169 m, 737 s. ^{1}H NMR spectrum, δ, ppm: 3.83 s (3H, OMe), 7.20 s (2H, H_{arom}, *J* 7.5 Hz), 7.28 t (2H, H_{arom}, *J* 7.5 Hz), 7.35–7.44 m (5H, H_{arom}), 7.52–7.55 m (2H, H_{arom}), 7.91 d (2H, H_{arom}, *J* 7.7 Hz). ^{13}C NMR spectrum, δ, ppm: 40.5 (C^{3}), 52.5 (OMe), 105.9 (C^{2}), 120.1 (2C_{arom}), 121.1 (2C_{arom}), 124.5 (C^{1}), 126.9 (2C_{arom}), 127.2 (2C_{arom}), 129.1 (2C_{arom}), 131.7 (2C_{arom}), 131.9 (C^{2}), 132.0 (C_{arom}), 140.5 (C_{arom}), 145.7 (C_{arom}), 159.9 (C=O). Found, %: C 85.13; H 4.89. $C_{23}H_{16}O_2$. Calculated, %: C 85.16; H 4.97.

Methyl 2-phenylpyrazolo[1,5-*f*]phenanthridine-3-carboxylate (6). Yield 1.35 g (92%), colorless crystals, mp 177–178°C (benzene). IR spectrum, ν, cm^{-1}: 1717 vs (C=O), 1531 m, 1451 m, 1327 m, 1273 m, 1130 s, 748 m, 706 m. ^{1}H NMR spectrum, δ, ppm: 3.84 s (3H, OMe), 7.45–7.54 m (4H, H_{arom}), 7.56–7.64 m (3H, H_{arom}), 7.76 d (2H, H_{arom}, *J* 8.2 Hz), 8.32 t (2H, H_{arom}, *J* 8.3 Hz), 8.66 d (1H, H_{arom}, *J* 8.3 Hz), 8.87 d (1H, H_{arom}, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 52.0 (OMe), 107.2 (C^{4a}), 117.1 (CH_{arom}), 121.5 (C^{4a}), 122.6 (CH_{arom}), 123.1 (2C_{arom}), 125.8 (CH_{arom}), 126.3 (CH_{arom}), 127.9 (C_{arom}), 128.25 (CH_{arom}), 128.29 (2CH_{arom}), 128.6 (CH_{arom}), 129.0 (2CH_{arom}), 129.3 (CH_{arom}), 129.4 (CH_{arom}), 133.1 (C_{arom}), 133.5 (C_{arom}), 137.3 (C_{arom}), 154.0 (C_{arom}), 166.7 (C=O). Found, %: C 78.35; H 4.64; N 7.86. $C_{23}H_{16}N_2O_2$. Calculated, %: C 78.39; H 4.58; N 7.95.

Methyl 3-methyl-2*H*-dibenzo[*e,g*]indazole-2-carboxylate (7a). A solution of 70 mg of 4*H*-pyrazole **4a** in 3 mL of anhydrous benzene was heated in a microwave reactor at 190°C for 40 min. After cooling the precipitated crystals were filtered off, washed with 10 mL of ethyl ether. Yield 15 mg (21%), mp 184–185°C. IR spectrum, ν, cm^{-1}: 1747 vs (C=O), 1450 m, 1431 s, 1354 s, 1331 s, 1277 m, 1246 m, 764 s, 725 m. ^{1}H NMR spectrum, δ, ppm: 3.19 d (3H, Me, *J* 1.2 Hz), 4.07 s (3H, OMe), 7.50–7.65 m (4H, H_{arom}), 8.20–8.22 m (1H, H_{arom}), 8.42 t (1H, H_{arom}, *J* 8.2 Hz), 8.46 m (1H, H_{arom}), 8.61 d (1H, H_{arom}, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 14.7 (Me), 52.2 (OMe), 116.4 (C^{3}), 123.4 (C_{arom}), 124.13 (C_{arom}), 124.15 (2C_{arom}), 124.22

($2C_{arom}$), 125.1 (C_{arom}), 126.5 (C_{arom}), 127.7 ($2C_{arom}$), 129.2 (C_{arom}), 132.1 (C_{arom}), 139.4 (C^4), 148.3 (C^2), 151.9 (C=O). Found, %: C 74.49; H 4.84; N 9.68. C18H14N2O2. Calculated, %: C 74.47; H 4.86; N 9.65.

3-Methyl-2*H*-dibenzo[*e,g*]indazole (8a). *a*. A solution of 0.2 g (0.66 mmol) of 4*H*-pyrazole **4a** in 5 mL of anhydrous methanol was heated in a microwave reactor at 160°C for 20 min. The precipitated crystals were filtered off. Yield 150 mg (81%), mp 259–260°C. IR spectrum, ν, cm^{-1}: 3121 br.m, 1613 m, 1547 m, 1524 m, 1443 m, 1316 m, 1161 m, 1046 m, 1007 m, 752 vs, 725 vs, 613 m, 428 m. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.82 s (CH_3), 3.55 t (1H, H_{arom}, *J* 7.9 Hz), 7.65–7.71 m (3H, H_{arom}), 8.28 d (1H, H_{arom}, *J* 7.9 Hz), 8.43–8.47 m (1H, H_{arom}), 8.76 t (1H, H_{arom}, *J* 7.4 Hz), the proton signals of NH group were not found. ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.6 (CH_3), 112.7 (C_{arom}), 122.2 (CH_{arom}), 123.1 (CH_{arom}), 123.9 ($2CH_{arom}$), 124.4 (CH_{arom}), 127.0 (CH_{arom}), 127.1 (C_{arom}), 127.2 (CH_{arom}), 127.5 (CH_{arom}), 128.0 (C_{arom}), 129.6 (C_{arom}), hydrogen-free carbon atoms of pyrazole fragment cannot be identified properly due to quick tautomeric transformations of compound **8a**. Found, %: C 82.69; H 5.41; N 11.98. $C_{16}H_{12}N_2$. Calculated, %: C 82.73; H 5.21; N 12.06.

b. In alternative experiment from 0.3 g (0.8 mmol) of sulfonyl-substituted 4*H*-pyrazole **13** [8] at heating in methanol at 160°C 190 mg (69%) of compound **8a** were obtained.

Thermal transformations of 4*H*-pyrazole (4b) in aprotic solvents. In 10 mL of anhydrous benzene or toluene 0.2 g (0.66 mmol) of 4*H*-pyrazole **4b** was heated for desired time. After removing the solvent in a vacuum the residue was analyzed by NMR. At boiling in benzene during 12 h a mixture was obtained of compounds **4b** and **9**, 1 : 1, after 1 h in benzene at 100°C, 3 : 7; after 20 min of heating in benzene at 130°C a full conversion was observed, compounds **7b** and **9** formed, 1 : 1; in toluene at 135°C after heating for 2.5 h a mixture was obtained of indazole **7b**, 3*H*-pyrazole **9**, and cyclopropene **5b**, 1.5 : 1.5 : 1, which were identified in the reaction mixture by ^{13}C NMR spectra.

Methyl 3-phenyl-2*H*-dibenzo[*e,g*]indazole-2-carboxylate (7b) was isolated by flash-chromatography on silica gel from the reaction mixture, obtained at thermolysis of 4*H*-pyrazole **4b** in benzene at 130°C. Yield 80 mg (38%). Colorless needle ctystals, mp 186–187°C (petroleum ether–ethyl acetate, 4 : 1). IR spectrum, ν, cm^{-1}: 3441 br.s, 1759 vs, 1651 s, 1632 s, 1447 s, 1339 vs, 1242 s, 1177 s, 1007 s, 833 s, 745 s, 718 s, 617 m, 475 m. ^{1}H NMR spectrum, δ, ppm: 4.01 s (3H, OMe), 7.12 t (1H, H_{arom}, *J* 8.0 Hz), 7.35 d (1H, H_{arom}, *J* 8.2 Hz), 7.43 t (1H, H_{arom}, *J* 8.3 Hz), 7.50–7.54 m (2H, H_{arom}), 7.68 t (1H, H_{arom}, *J* 8.1 Hz), 8.46 t (2H, H_{arom}, *J* 7.3 Hz), 8.73 d (1H, H_{arom}, *J* 7.5 Hz). ^{13}C NMR spectrum, δ, ppm: 55.2 (OMe), 117.5 (C_{arom}), 123.6 (CH_{arom}), 123.9 (CH_{arom}), 124.2 (CH_{arom}), 124.4 (CH_{arom}), 125.0 (C_{arom}), 126.9 (C_{arom}), 127.0 (CH_{arom}), 127.5 (CH_{arom}), 127.8 (CH_{arom}), 129.2 ($2CH_{arom}$), 129.3 (CH_{arom}), 129.57 (CH_{arom}), 129.61 ($2CH_{arom}$), 130.1 (C_{arom}), 132.16 (C_{arom}), 132.23 (C_{arom}), 141.0 (C^5), 148.4 (C^4), 150.9 (C=O). Found, %: C 78.40; H 4.63; N 7.97. C23H16N2O2. Calculated, %: C 78.39; H 4.58; N 7.95.

Methyl 3-phenyl-3*H*-dibenzo[*e,g*]indazole-3-carboxylate (9). A solution of 1.48 g (4.2 mmol) of 4*H*-pyrazole **4b** in 3 mL of anhydrous toluene was boiled for 2 h, monitoring disappearance of initial compound by TLC. The solvent was removed at a lowered pressure, the residue was purified by crystallization. Yield 92 mg (62%), colorless crystals, mp 159–160°C (ethyl ether).[1] IR spectrum, ν, cm^{-1}: 1736 vs (C=O), 1454 m, 1234 s, 1122 w, 1006 m, 802 w, 752 m, 725 m, 520 w, ^{1}H NMR spectrum, δ, ppm: 3.49 s (3H, OMe), 7.34–7.39 m (5H, H_{arom}), 7.66 t (1H, H_{arom}*J* 8.2 Hz), 7.78–7.82 m (1H, H_{arom}), 7.86–7.90 m (2H H_{arom}), 8.07 t (1H, H_{arom}*J* 8.2 Hz), 8.81–8.87 m (2H, H_{arom}), 9.12–9.15 m (1H, H_{arom}*J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 53.7 (OMe), 105.0 (C^3), 123.4 (CH_{arom}), 123.9 (CH_{arom}), 124.8 (CH_{arom}), 125.0 (C_{arom}), 126.7 (C_{arom}), 128.1 (CH_{arom}), 128.3 (CH_{arom}), 128.5 (CH_{arom}), 128.7 (CH_{arom}), 128.8 ($2CH_{arom}$), 128.9 (CH_{arom}), 129.3 (CH_{arom}), 129.4 ($2CH_{arom}$), 131.6 (C_{arom}), 131.7 (C_{arom}), 132.4 (C^4), 135.8 (C_{arom}), 153.0 (C^5), 167.49 (C=O). Found, %: C 78.35; H 4.50; N 8.00. $C_{23}H_{16}N_2O_2$. Calculated, %: C 78.39; H 4.58; N 7.95.

Isomerization of 3*H*-pyrazole (2) in glacial acetic acid. To a solution of 1.55 g (4.4 mmol) of compound **2** in 10 mL of glacial acetic acid was added 2 drops of conc. H_2SO_4. The mixture was kept at 20°C for 6 h, then diluted with 50 mL of water. The precipitated crystals were filtered off and crystallized from

[1] In [14] at thermolysis of 3*H*-pyrazole **2** in glacial acetic acid a single product was obtained, mp 159°C, which was erroneously identified as 1*H*-pyrazole **7b**

methanol. We obtained 0.73 g (47%) of 3*H*-pyrazole **9**, mp 159–160°C.

X-ray diffraction analysis of single crystals of compounds 4b, 6, 7a, and 18. Crystallographic characteristics, parameters of XRD experiment and of structure refinement are compiled in the table, their spatial arrangement is demonstrated in figures 1–4. In each case the initial fragment of structure was solved by the direct method using software SHELX [25]. Positions of the remaining nonhydrogen atoms were determined by the differential synthesis of electron density and refined by the least squares method with respect to $|F|^2$ in an anisotropic approximation for thermal parameters. In the structure **18** the positions of hydrogen atoms were determined geometrically, the parameters were refined in the *rider* model. The positions of hydrogen atoms in pyrazole **7a** were found from the differential synthesis of electron density, their parameters were refined as free in isotropic approximation in the general least squares method cycle. Results of XRD investigations of pyrazoles **4b**, **7a**, **6**, and **18** were deposited to Cambridge Crystallographic Data Centre (CCDC nos. 1515374, 1486265, 1531656, 1530680 respectively). Molecular graphics was performed with software ORTEP-3 [28].

ACKNOWLEDGMENTS

This study was performed in the framework of the basic part of State task for high schools and scientific organizations in the field of research (project no. 3.6502.2017/BCh).

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