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Regioselectivity of the Thermal van Alphen–Hüttel Rearrangement of 4- and 5-Mono- and 4,5-Disubstituted 3,3-Diphenyl-3*H*-pyrazoles

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Abstract—Thermal van Alphen–Hüttel rearrangement of methyl 3,3-diphenyl-3*H*-pyrazole-4-carboxylate, 3,3-diphenyl-3*H*-pyrazole-4-carbonitrile, and methyl 5-methyl-3,3-diphenyl-3*H*-pyrazole-4-carboxylate involves completely regioselective migration of one phenyl group from the 3-position to N^2 with formation of aromatic 1*H*-pyrazole system. Thermal rearrangement of methyl 3,3-diphenyl-3*H*-pyrazole-5-carboxylate leads to the formation of methyl 4,5-diphenyl-1*H*-pyrazole-3-carboxylate as a result of migration of the 3-phenyl group exclusively to the C^4 atom and subsequent prototropic isomerization. Under analogous conditions, methyl 4-methyl-3,3-diphenyl-3*H*-pyrazole-5-carboxylate, methyl 5-(methanesulfonyl)-3,3-diphenyl-3*H*-pyrazole-4-carboxylate, methyl 5-(benzenesulfonyl)-3,3-diphenyl-3*H*-pyrazole-4-carboxylate, and dimethyl 3,3-diphenyl-3*H*-pyrazole-4,5-dicarboxylate have been regioselectively converted into the corresponding 4*H*-pyrazoles. Thermolysis of 5-(4-methylbenzenesulfonyl)-3,3-diphenyl-3*H*-pyrazole-4-carbonitrile gives rise to a mixture of 1*H*- and 4*H*-pyrazoles, the former considerably prevailing, whereas the corresponding 1*H*-pyrazoles are formed as the only product from 5-(methanesulfonyl)- and 5-(benzenesulfonyl)-3,3-diphenyl-3*H*-pyrazole-4-carbonitriles.

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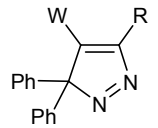
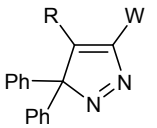
It is known [1] that 3,3-disubstituted 3*H*-pyrazoles undergo thermal or acid-catalyzed 1,5-sigmatropic van Alphen–Hüttel rearrangement [2, 3] into 1*H*- and/or 4*H*-pyrazoles. Despite higher stability of the aromatic 1*H*-pyrazole system relative to nonaromatic 4*H*-pyrazoles, the latter sometimes appear to be the major or only isomerization product [4]. Factors responsible for regioselectivity of this rearrangement remain so far the matter of discussion.

While trying to shed light on this problem, we compared the known results of thermal van Alphen–Hüttel rearrangement of three pairs of 4,5-disubstituted 3,3-diphenyl-3*H*-pyrazoles **1a**–**1c** and **2a**–**2c** differing by the nature of one electron-withdrawing substituent and its position, as well as of structurally related compound **1d** [5–8]. Pyrazoles **1a**–**1d** with the electron-withdrawing substituent on C^4 are mainly converted into *N*-phenyl-1*H*-pyrazole derivatives, whereas regioisomeric 5-W-substituted (W is an electron-withdrawing group) compounds **2a**–**2c** give rise preferentially to 4*H*-pyrazoles. The isomerization of sulfonyl-substituted 3*H*-pyrazoles **1a**, **1b**, **2a**, and **2b** is completely regioselective; the regioselectivity of the rearrangement of methoxycarbonyl and cyano compounds **1c**, **1d**, and **2c** is somewhat lower due to formation of minor alternative isomerization products.

We have also noticed that the thermolysis of two 3,3-diphenyl-3*H*-pyrazoles **3e** [9] and **3f** [10] containing an electron-withdrawing substituent in the 5-position and free 4-position is completely regioselective and is directed toward the corresponding 4*H*-pyrazole which undergoes fast prototropic isomerization into



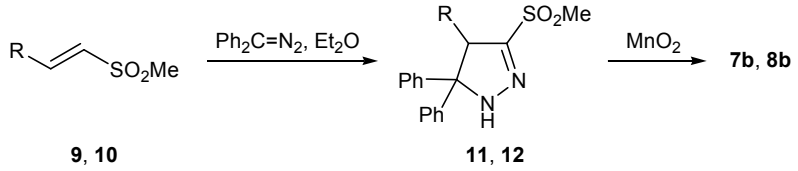
1a–1d, **4c**, **4d**, **5c**



2a–2c, **3c**, **3e–3j**, **6c**
7b, **7c**, **7k**, **8a**, **8b**, **8k**

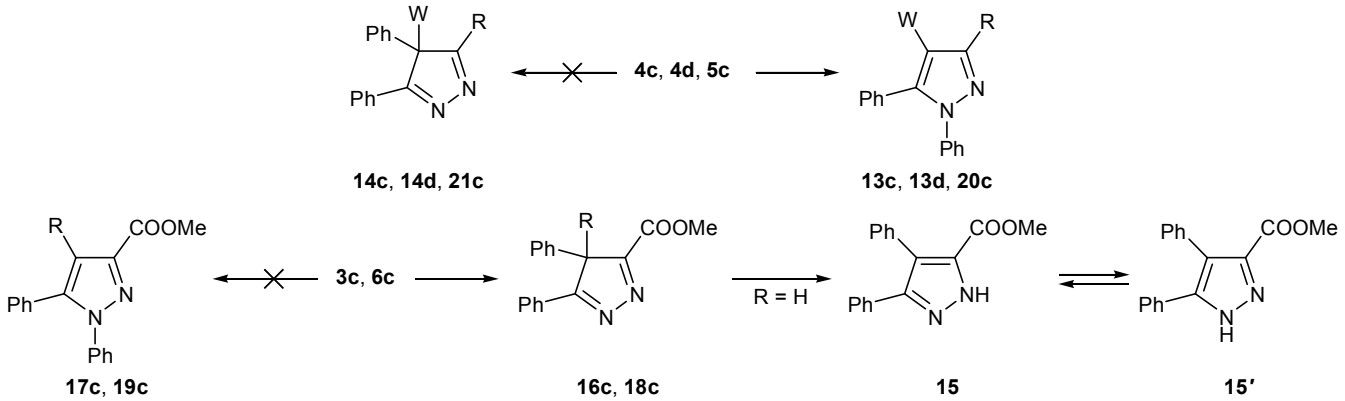
1, **2**, R = Ph; **3**, **4**, R = H; **5**, **6**, R = Me; **7**, R = COOMe; **8**, R = CN; hereinafter, W = Ts (**a**), SO_2Me (**b**), COOMe (**c**), CN (**d**), Ac (**e**), $P(O)Ph_2$ (**f**), Me (**g**), Ph (**h**), cycloalk-1-en-1-yl (**i**), H (**j**), SO_2Ph (**k**).

Scheme 1.



9, **11**, R = COOMe; **10**, **12**, R = CN.

Scheme 2.



13, **14**, **16**, **17**, R = H; **18**–**21**, R = Me.

1*H*-pyrazole derivative. On the other hand, analogous regioselectivity is observed in the isomerization of 3,3-diphenyl-3*H*-pyrazoles **3g** [11], **3h** [12, 13], and **3i** [14] with a hydrocarbon substituent on C^5 and free 4-position. Finally, it is known [15] that 3,3-diphenyl-3*H*-pyrazole (**3j**) having no substituents in positions *4* and *5* rearranges into 1*H*-pyrazole through intermediate 4*H*-pyrazole. We have found no published data on 4-substituted 3,3-diphenyl-3*H*-pyrazoles with no substituent on C^5 and their thermal transformations.

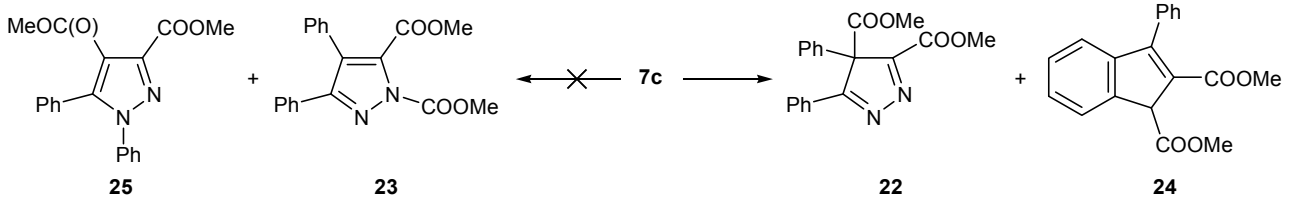
The present study was aimed at elucidating the effect of the nature of substituents and their position in 3,3-diphenyl-3*H*-pyrazoles on the direction of thermal 1,5-sigmatropic shift of the phenyl group from C^3. For this purpose, the substrate series was considerably extended by including three 4- and 5-monosubstituted 3,3-diphenyl-3*H*-pyrazoles: 5-methoxycarbonyl derivative **3c** and 4-methoxycarbonyl and 4-cyano derivatives **4c** and **4d**, as well as eight 4,5-disubstituted 3,3-diphenyl-3*H*-pyrazoles, namely two regioisomeric compounds **5c** and **6c** with one electron-withdrawing substituent and pyrazoles **7b**, **7c**, **7k**, **8a**, **8b**, and **8k** possessing two electron-withdrawing substituents.

Initial 3*H*-pyrazoles **3s**, **4c**, **4d**, **7k**, **8a**, and **8k** were synthesized according to the procedures reported in [16], compounds **5c** and **6c** were prepared as described in [17], and pyrazole **7c** was synthesized according to [18]. 3*H*-Pyrazoles **7b** and **8b** were not reported previously; they were synthesized in this work in two steps starting from methyl 3-(methanesulfonyl)prop-2-enoate (**9**) and 3-(methanesulfonyl)prop-2-enenitrile (**10**), respectively, through 4,5-dihydro-1*H*-pyrazoles **11** and **12** (Scheme 1, see [16]). The structure of **7b**, **8b**, **11**, and **12** was confirmed by IR and ^1H and ^{13}C NMR spectra with account taken of spectral parameters of model arenesulfonyl-substituted analogs [16].

Initially, we studied thermal transformations of 3*H*-pyrazoles **3c**, **4c**, and **4d**. When pyrazoles **4c** and **4d** with an acceptor substituent on C^4 were heated in boiling toluene for 1 h, completely regioselective 1,5-sigmatropic shift of one phenyl group from C^3 to N^2 was observed with formation of known *N*-phenyl-1*H*-pyrazoles **13c** [19] and **13d** [20, 21] (Scheme 2). Thermolysis of 5-(methoxycarbonyl) derivative **3c** under analogous conditions was reported to produce 1*H*-pyrazole **15** [18]. We have reproduced this experiment and reliably characterized compound **15** by spectral data.[1] Obviously, this result should be treated as tandem 1,5-phenyl shift to C^4 and proton transfer to

[1] Pyrazole **15** in solution exists in equilibrium with tautomer **15′** (Scheme 2), which is reflected in the ^{13}C NMR spectrum by broadening of signals from carbon atoms of the five-membered heterocycle and averaging of signals from carbon atoms of the two nonequivalent benzene rings.

Scheme 3.



25 **23** **22** **24**

the nitrogen atom. The second step of this process is very fast, and intermediate 4*H*-pyrazole **16c** could not be detected.

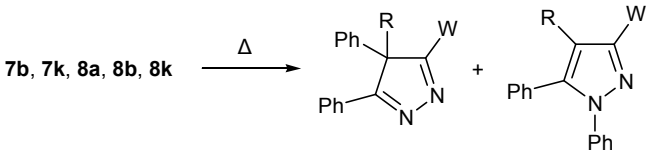
Undoubtedly, it was interesting to compare the directions of isomerization of regioisomeric 3*H*-pyrazoles **5c** and **6c** (homologs of the **3c**/**4c** pair and analogs of the **1c**/**2c** pair). The transformation of **6c** into 4*H*-pyrazole **18c** as a result of 1,5-phenyl shift toward C^4 was described in [17]. We also obtained compound **18c** under the conditions reported in [17], and its spectral parameters coincided with those given in [7]. The thermal rearrangement of **5c** (benzene, microwave reactor, 140°C, 40 min) afforded known *N*-phenyl-3*H*-pyrazole **20c** [22] as the only product.[2] Our results indicated similarity in the behavior of regioisomeric couples **5c**/**6c** and **3c**/**4c** in the van Alphen–Hüttel rearrangement, but the transformations of **1c** and **2c** were less selective, indicating somewhat different effects of methyl and phenyl groups on the isomerization direction.

We then turned to the thermal isomerization of 3*H*-pyrazole **7c** having two similar electron-withdrawing substituents (methoxycarbonyl groups) on C^4 and C^5. The transformation of **7c** into **22** was described by Baumes et al. [24], and the structure of **22** was determined by chemical methods. Simultaneously, the authors [24] corrected the results of [18, 25], where the thermolysis product of **7c** was assigned the structure of *N*-(methoxycarbonyl)-1*H*-pyrazole **23**. In these studies [18, 24, 25], the isomerization was carried out by heating in acetic acid, which did not ruled out acid catalysis. Therefore, we tried to accomplish purely thermal isomerization of 3*H*-pyrazole **7c**. By heating compound **7c** in boiling ethanol for 40 min we also obtained 4*H*-pyrazole **22** with a small impurity (5–8%) of known indene **24** [26, 27] (Scheme 3). The same 4*H*-pyrazole **22** was formed in a mixture with **24** at a ratio of 1:1.3 (according to the ^{1}H NMR data) when compound **7c** was refluxed in toluene for 1 h. No diester **25** that could result from migration of phenyl group to N^2 was detected. While reproducing the results of [18, 24, 25] on acid-catalyzed isomerization of **7c** we also isolated 4*H*-pyrazole **22** as the only product which remained unchanged after prolonged (8 h) heating in glacial acetic acid. The UV spectrum of **22** provided an additional support of its structure (cf. the data for its analog **18c** [17]). Almost identical UV spectrum (λ_{max} 314 nm, logε 4.13) was erroneously considered in [25] as an evidence for the structure of **23**.

Compounds **22** and **24** were isolated as crystalline substances by silica gel column chromatography. The structure of **22** follows from its ^{1}H and ^{13}C NMR spectra. In particular, signals of C^3 and C^5 deshielded by the effect of nitrogen atoms appeared in the ^{13}C NMR spectrum at δ_C 168.0 and 175.4 ppm, which is typical of such compounds [1, 5, 7, 17]. We believe that indene **24** is formed from 3*H*-pyrazole **7c** via denitrogenation through intermediate cyclopropene (cf. [5]), which is concurrent to the van Alphen–Hüttel rearrangement.

In the next step of our study we examined thermal van Alphen–Hüttel rearrangement of 4,5-disubstituted 3*H*-pyrazoles **7b**, **8a**, **8b**, and **8k** containing different electron-withdrawing groups on C^4 and C^5. Compound **7k** was completely converted into 4*H*-pyrazole **26k** on heating in boiling benzene for 10 min [16]. Analogous isomerization of **7b** into **26b** in boiling benzene was complete in 40–80 min. 3*H*-Pyrazole **8a** gave rise to a mixture of 4*H*- and 1*H*-pyrazoles **27a** and **28a** at a ratio of 1:3 on heating in CCl_4 for 1 h. The rearrangement of 3*H*-pyrazoles **8b** and **8k** was more selective, and 1*H*-pyrazoles **28b** and **28k** were the only products (Scheme 4).

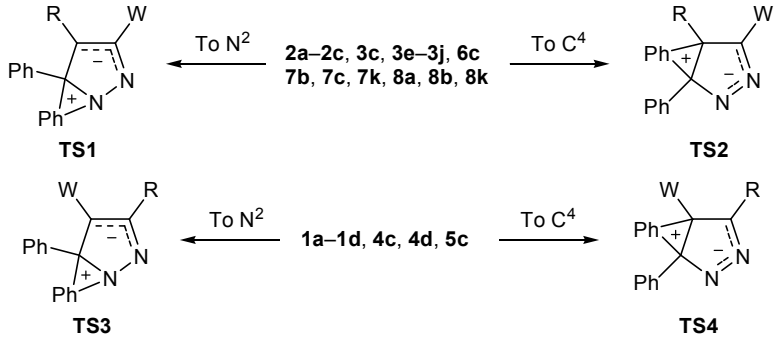
Scheme 4.



26b, **26k**, **27a** **28a**, **28b**,**28k**

[2] Analogous result (i.e., exclusive formation of *N*-phenyl-1*H*-pyrazole derivative) was obtained in [23] in the thermolysis of ethyl 3,3-diphenyl-3*H*-pyrazole-5-carboxylate (analog of **5c**).

Scheme 5.



4*H*-Pyrazoles **26b** and **26k** and 1*H*-pyrazoles **28a**, **28b**, and **28k** were isolated in the crystalline state and characterized by spectral data. Compounds **28a**, **28b**, and **28k** showed in the ^{13}C NMR spectra C^3 and C^5 signals typical of 1*H*-pyrazoles at δ_C ~146 and 152 ppm, which is consistent with published data for structurally related compounds [5, 7]. We failed to isolate 4*H*-pyrazole **27a** which was detected in the reaction mixture by ^{13}C NMR (δ_{C^4} ~80 ppm and downfield signals of C^3 and C^5, see above).

Thus, the major pathway of the thermolysis of 3*H*-pyrazoles **2a**–**2c**, **3c**, **3e**–**3j**, **6c**, **7b**, **7c**, and **7k** is 1,5-phenyl shift to C^4, whereas 3-phenyl group in 3*H*-pyrazoles **1a**–**1d**, **4c**, **4d**, **5c**, **8a**, **8b**, and **8k** preferentially migrates to N^2. We previously [5, 7] proposed a qualitative interpretation of the regioselectivity in the isomerization of 3,3-diphenyl-3*H*-pyrazoles **1a**–**1d** and **2a**–**2c**, according to which transition states for each of the two possible isomerization pathways is postulated to be equivalent to the π-system of the corresponding nonalternant diazabicyclo[3.1.0]-hexatriene.[3] Let us consider to which extent this approach is applicable for the prediction of the isomerization direction of 3*H*-pyrazoles listed above. The transition states for both isomerization pathways are denoted as **TS1**–**TS4** (Scheme 5). All these transition states are dipolar ions, and charge distribution therein is estimated by the Hückel molecular orbital (HMO) method for the bicyclo[3.1.0]hexatriene π-system [29]: the negative charge is delocalized over the allylic fragment where the terminal atoms possess the main charge, and the middle atom bears a minor negative charge; the positive charge is delocalized over the three-membered ring. Obviously, such dipolar ion should be sensitive to electronic effects of substituents in positions *4* and *5*, as well as to the position of nitrogen atoms.

Let us consider first those 3*H*-pyrazoles whose isomerization leads to 4*H*-pyrazoles, in particular 4,5-unsubstituted compound **3j** and 5-monosubstituted derivatives **3c**, and **3e**–**3i**. Transition state **TS2** for pyrazoles **3j** and **3g** is more stable than **TS2** due to the presence of two electronegative nitrogen atoms in the negatively charged moiety. Transition state **TS1** contains only one nitrogen atom in the negatively charged moiety, whereas the second nitrogen atom resides in the positively charged moiety, so that **TS1** is destabilized. 4,5-Disubstituted 3*H*-pyrazoles **2a**, **2b**, and **6c** with one electron-withdrawing substituent on C^5 show analogous complete regioselectivity, which is not surprising since **TS2** is additionally stabilized by increased electronegativity of the terminal allylic carbon atom bearing an electron-withdrawing substituent. Somewhat unexpectedly, pyrazole **2c** displayed lower regioselectivity.

Consider next transition states for the rearrangement of pyrazoles **7b**, **7c**, **7k**, **8a**, **8b**, and **8k** possessing two electron-withdrawing substituents on C^4 and C^5. It was difficult to determine whether **TS1** or **TS2** is preferred for pyrazole **7c**. In this case, two structural factors act in the opposite directions: favorable arrangement of the nitrogen atoms stabilizes **TS2**, whereas two identical electron-withdrawing methoxycarbonyl groups stabilize **TS1** to a greater extent. The different regioselectivities of the isomerization of **7b**, **7k**, **8a**, **8b**, and **8k** are determined by the different strengths of the electron-withdrawing substituent W on C^4. The rearrangement of **7b** and **7k** through **TS2** is preferred due to stabilizing effect of the strong electron-withdrawing sulfonyl group (W), which compensates for destabilizing effect of relatively weak electron-withdrawing methoxycarbonyl group (R). In the case of pyrazoles **8a**, **8b**, and **8k**, **TS1** becomes

[3] Analogous approach based on the Dewar molecular orbital perturbation theory of pericyclic reactions [28] was proposed in [29] to interpret 1,5-hydride shift in cyclopentadiene.

preferable since strong electron-withdrawing cyano group (R) simultaneously destabilizes **TS2** {cf. Hammett constants σ^- and σ_I: 1.13 and 0.59 (CO_2Me), 1.00 and 0.57 (CN), 0.74 and 0.32 (COOMe) [30]}. Analogous result (i.e., the formation of the corresponding *N*-phenyl-1*H*-pyrazole) was obtained previously [10] in the thermolysis of 4,5-bis(diphenylphosphoryl)-3,3-diphenyl-3*H*-pyrazole containing a stronger (than methoxycarbonyl) electron-withdrawing substituent on C^4, which is structurally related to **7c**.

3*H*-Pyrazoles **1a**–**1d**, **4c**, **4d**, and **5c** possessing one electron-withdrawing substituent in the 4-position are converted mainly into *N*-phenyl-1*H*-pyrazoles. The relative stability of the corresponding transition states **TS3** and **TS4** cannot be estimated because of opposite effects of two structural factors: position of nitrogen atoms and electron-withdrawing effect of the 4-substituent. Nevertheless, it is possible to correlate the stability of transition states with the experimental data assuming better stabilization of **TS3** by the substituent W and destabilization of **TS4** by the same substituent.

The lower regioselectivity of the rearrangement of **1c** and **1d** may be attributed to the relatively weak electron-withdrawing effect of the substituent W in combination with stabilization of **TS4** by the phenyl substituent capable of acting as a weak acceptor (σ^- = 0.02, σ_I = 0.12 [30]).

Calculated (DFT/PBE) activation barriers to the transformation of 3*H*-pyrazoles into 1*H*- and 4*H*-pyrazoles and relative energies of the transformation products[a]

3*H*-Pyrazole no.	Activation barrier, kcal/mol		Relative energy,[b] kcal/mol	
	to 4*H*-pyrazole	to 1*H*-pyrazole	4*H*-pyrazole	1*H*-pyrazole
1c	25.6	**22.4**	–10.3	–32.4
2c	**23.8**	24.1	–4.4	–33.3
3c	**19.5**	23.6	–13.0	–34.8
3d	**19.3**	23.2	–13.6	–34.6
3j	**22.0**	22.9	–13.8	–33.5
4c	26.0	**21.2**	–8.3	–35.0
4d	25.3	**22.9**	–5.4	–35.0
5c	25.9	**21.3**	–8.8	–33.5
6c	**23.8**	25.0	–6.5	–31.9
7c	**21.7**	22.3	–11.4	–35.4

[a] The total energies of all compounds and transition states were calculated with correction for zero-point vibration energy (*ZPE*).

[b] In all cases, the relative energies were calculated with respect to the corresponding 3*H*-pyrazole.

The proposed qualitative HMO interpretation of the experimentally observed differences in the regioselectivity of thermal van Alphen–Hüttel rearrangement of 3*H*-pyrazoles in relation to the position and nature of substituents therein is quite consistent with the results of DFT/PBE calculations (PRIRODA 06) of the activation barriers for the two isomerization pathways of 3*H*-pyrazoles **1c**–**7c**, **3d**, **3j**, and **4d**, leading to 4*H*-pyrazoles and *N*-phenyl-1*H*-pyrazoles, and of the relative energies of the transformation products (see table). In all cases, the 1,5-phenyl shift products were more stable than the initial 3*H*-pyrazoles, but to considerably different extents. 4*H*-Pyrazoles were more stable by 5–13 kcal/mol, and *N*-phenyl-1*H*-pyrazoles, by 32–35 kcal/mol. This difference seems to be quite reasonable taking into account aromaticity of the 1*H*-pyrazole system. It may be concluded that the isomerization of 3*H*-pyrazoles into less stable 4*H*-pyrazole should be kinetically controlled, i.e., the activation barrier to this transformation showed be lower than the barrier to the isomerization into 1*H*-pyrazole.

In fact, the calculated activation barrier to the rearrangement of 3,3-diphenyl-3*H*-pyrazole **3j** into 4*H*-pyrazole is lower by only 0.6 kcal/mol than that to the transformation into *N*-phenyl-1*H*-pyrazole. This result indicates quite small contribution of the effect of the position of nitrogen atoms (see above). The barrier to the transformation of 3*H*-pyrazole **4c** into aromatic *N*-phenyl-1*H*-pyrazole **13c** is lower by 4.8 kcal/mol than that to the transformation into 4*H*-pyrazole **14c**. On the other hand, the barrier to the isomerization of **3c** into thermodynamically less stable 4*H*-pyrazole **16c** is lower by 4.1 kcal/mol than the barrier to the transformation into *N*-phenyl-1*H*-pyrazole **17c** (Fig. 1).

Largely similar situation is observed in the rearrangements of 3*H*-pyrazoles **3d**,[4] and **4d**. Here, the energy differences between the transition states are 2.6 kcal/mol in favor of *N*-phenyl-1*H*-pyrazole **13d** for **4d** and 3.9 kcal/mol in favor of 4*H*-pyrazole **16d** for **3d**. The activation barrier to the transformation of 4,5-disubstituted 3*H*-pyrazole **5c** into *N*-phenyl-1*H*-pyrazole **20c** is lower by 4.6 kcal/mol than that found for the alternative pathway, i.e., the situation is approximately similar to that observed for **4c**. The barrier to the transformation of **6c** into **19c** is lower by only 1.2 kcal/mol than into *N*-phenyl-1*H*-pyrazole **18c**. This difference is considerably smaller than that in the rearrangement of monosubstituted analog **3c**, though (in

[4] There are no published data on the synthesis and thermal isomerization of 3*H*-pyrazole **3d**.

terms of the qualitative model) the 4-methyl group in **6c** should provide additional stabilization of the transition state leading to 4*H*-pyrazole, as compared to **3c**. As concerns pyrazole **7c**, its isomerization into **22** (Fig. 2) is more favorable by only 0.6 kcal/mol.

The results of calculations for 3*H*-pyrazoles **1c** and **2c** are noticeable. These compounds showed the opposite but incomplete regioselectivity of the van Alphen–Hüttel rearrangement. The calculated barriers for the transformation of **2c** were in a good agreement with the experimental data. The rearrangement of **2c** into 4*H*-pyrazole is more favorable than the isomerization into 1*H*-pyrazole by only 0.3 kcal/mol. However, the calculations performed for 3*H*-pyrazole **1c** predict preferential formation of 1*H*-pyrazole (the corresponding activation barrier is lower by 3.2 kcal/mol). This is less consistent with the experimental data [6, 7, 31], according to which the fraction of 4*H*-pyrazole derivative is appreciable. Presumably, the formation of 4*H*-pyrazole from **1c** is determined by the contribution of the acid-catalyzed isomerization leading exclusively to 4*H*-pyrazole[5] rather than by lower regioselectivity of the thermal isomerization of **1c**. We performed thermolysis of **1c** under the conditions described in [7] but with addition of triethylamine in order to eliminate possible traces of mineral acid from the reaction mixture or reactor surface. However, the product ratio did not change and was ~4 : 1 in favor of 1*H*-pyrazole. Therefore, the reason for the observed inconsistency between the calculated and experimental data remains unclear.

Thus, though quantum chemical calculations were performed only for some selected 3,3-diphenyl-3*H*-pyrazoles, their results in combination with qualitative HMO analysis of the transition states generally make it possible to predict regioselectivity of the thermal van Alphen–Hüttel 1,5-sigmatropic rearrangement of these compounds with a high probability. The regioselectivity of this rearrangement is largely determined by the ability of substituents in positions *4* and *5* of 3,3-diphenyl-3*H*-pyrazoles to stabilize the corresponding transition states.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a JEOL ECX-400 spectrometer at 400 and 100 MHz, respectively. The IR spectra were recorded in KBr on an InfraLYuM FT-02 spectrometer with Fourier transform. The UV spectra were measured on a Shimadzu UV-2600 spectrophotometer and were processed using UV Probe 2.4. The elemental analyses were obtained on a VarioMICRO CHNS analyzer. Analytical TLC was performed on Sorbfil plates with light petroleum ether–acetone (4 : 1) as eluent; the chromatograms were developed in a iodine chamber. The melting points were determined in glass capillaries on a Mettler Toledo MP-50 melting point analyzer.

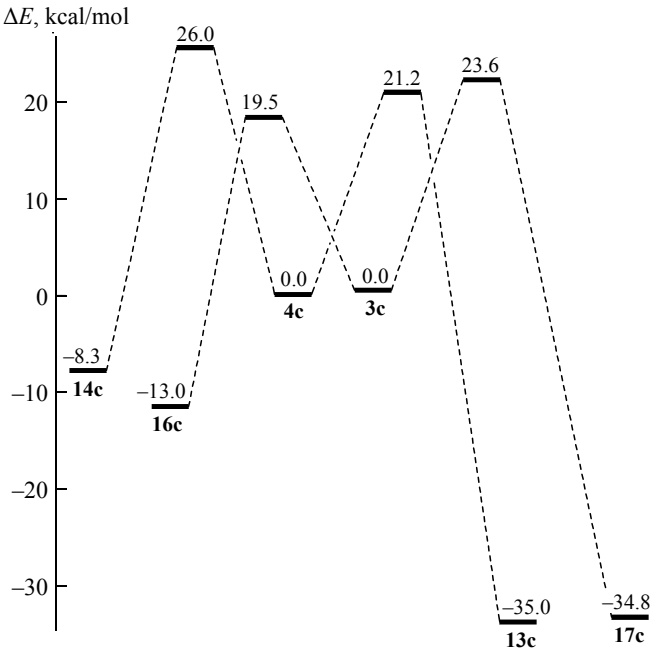


Fig. 1. Calculated (DFT/PBE) energy profiles for the transformations of 3*H*-pyrazoles **3c** and **4c** into 1*H*- and 4*H*-pyrazoles **13c**, **14c**, **16c**, and **17c**.

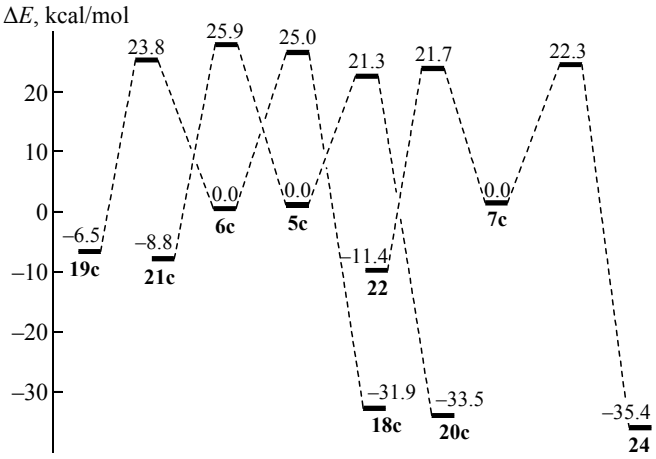


Fig. 2. Calculated (DFT/PBE) energy profiles for the transformations of 3*H*-pyrazoles **5c**–**7c** into compounds **18c**–**21c**, **22**, and **24**.

[5] When 3*H*-pyrazole **1c** was kept in glacial acetic acid in the presence of a catalytic amount of H_2SO_4 at 20°C, the corresponding 4*H*-pyrazole was formed with complete regioselectivity [7].

Quantum chemical calculations of pyrazole and transition state structures were carried out in several steps. First, initial sets of 1*H*-, 3*H*-, and 4*H*-pyrazole conformers were simulated by the MMFF94 method [32] using Marvin Beans 15.5.4 [33]. The structures of most favorable conformers were optimized at the RM1 level of theory [34] using MOPAC2012 [35]. The final structures were obtained in terms of the DFT/PBE approximation (PRIRODA 06 software [36], L1 basis set [37]). Transition states were localized by scanning the potential energy surface along the selected reaction coordinate and calculating the corresponding Hessian eigenvalues (one imaginary frequency); the transition states were verified by the intrinsic reaction coordinate (IRC) procedure in two directions.

3*H*-Pyrazoles **3c**, **4c**, **4d**, **8a**, and **8k** were synthesized according to the procedures described in [16]; diphenyldiazomethane was prepared as described in [38]. Commercial dimethyl acetylenedicarboxylate and methanesulfonyl chloride (from Aldrich) were used.

Methyl 5-methyl-3,3-diphenyl-3*H*-pyrazole-4-carboxylate (5c) was synthesized as described in [17]. ^{1}H NMR spectrum, δ, ppm: 2.82 s (3H, Me), 3.73 s (3H, OMe), 7.16–7.20 m (4H, H_{arom}), 7.28–7.34 m (6H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.4 (Me), 52.2 (OMe), 108.5 (C^3), 128.45 (4C, C_{arom}), 128.53 (2C, C_{arom}), 128.7 (4C, C_{arom}), 135.1 (2C, C_{arom}), 139.7 (C^4), 160.6 (C^5), 163.2 (C=O).

Oxidative dehydrogenation of dihydropyrazoles 11 and 12 (*general procedure*). Activated manganese(IV) oxide [39], 2.6 g (30 mmol), was added to a solution of 1.5 mmol of compound **11** or **12** in 40 mL of a 1:3 mixture of anhydrous benzene and methylene chloride under continuous stirring in an argon atmosphere. The mixture was stirred for 48 h, filtered through a 1-cm layer of silica gel, and evaporated under reduced pressure on a rotary evaporator, and the residue was washed with light petroleum ether.

Methyl 5-(methanesulfonyl)-3,3-diphenyl-3*H*-pyrazole-4-carboxylate (7b). Yield 90%, light yellow crystals, mp 103–104°C. IR spectrum, ν, cm^{-1}: 1736 s, 1617 w, 1600 w, 1582 w, 1489 m, 1447 m, 1431 m, 1331 v.s, 1289 s, 1157 s, 1130 s, 957 m, 791 s, 760 m, 749 m, 702 m, 529 m, 498 m. ^{1}H NMR spectrum, δ, ppm: 3.42 s (3H, Me), 3.81 s (3H, OMe), 7.20–7.24 m (4H, H_{arom}), 7.34–7.43 m (6H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 43.1 (Me), 53.8 (OMe), 111.8 (C^3), 128.4 (4C, C_{arom}), 129.2 (4C, C_{arom}), 129.7 (2C, C_{arom}), 132.8 (2C, C_{arom}), 152.6 (C^4), 153.3 (C^5), 161.9 (C=O). Found, %: C 60.62; H 4.49; N 7.83; S 8.96. $C_{18}H_{16}N_2O_4S$. Calculated, %: C 60.66; H 4.53; N 7.86; S 9.00.

5-(Methanesulfonyl)-3,3-diphenyl-3*H*-pyrazole-4-carbonitrile (8b). Yield 71%, yellow crystals, mp 96–97°C (from Et_2O). IR spectrum, ν, cm^{-1}: 2924 w, 2215 w, 1493 m, 1451 m, 1408 w, 1339 v.s, 1150 v.s, 953 m, 775 s, 752 s, 694 s, 660 m, 640 w, 540 s, 517 m, 494 m. ^{1}H NMR spectrum, δ, ppm: 3.48 s (3H, Me), 7.29–7.32 m (4H, H_{arom}), 7.40–7.46 m (6H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 42.5 (Me), 110.1 (C^3), 112.0 (CN), 127.8 (4C, C_{arom}), 129.8 (4C, C_{arom}), 130.4 (2C, C_{arom}), 132.4 (2C, C_{arom}), 133.2 (C^4), 157.8 (C^5). Found, %: C 63.18; H 4.11; N 12.84; S 9.87. $C_{17}H_{13}N_3O_2S$. Calculated, %: C 63.14; H 4.05; N 12.99; S 9.91.

Dimethyl 3,3-diphenyl-3*H*-pyrazole-4,5-dicarboxylate (7c). A solution of 1 g (5.6 mmol) of diphenyldiazomethane in 10 mL of anhydrous diethyl ether was added to a solution of 0.73 g (5.1 mmol) of dimethyl acetylenedicarboxylate in 40 mL of anhydrous diethyl ether. The mixture was left to stand in a partially open flask, and yellow crystals separated as the solvent gradually evaporated. The crystals were filtered off. Yield 1.12 g (65%), mp 93–94°C (from Et_2O) [18]. IR spectrum, ν, cm^{-1}: 1748 s, 1725 v.s, 1651 w, 1497 w, 1435 m, 1339 m, 1316 m, 1277 m, 1242 m, 1204 m, 1142 m. ^{1}H NMR spectrum, δ, ppm: 3.77 s (3H, OMe), 4.02 s (3H, OMe), 7.20–7.24 m (4H, H_{arom}), 7.30–7.40 m (6H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 53.3 (2C, OMe), 110.5 (C^3), 128.4 (4C, C_{arom}), 129.0 w (4C, C_{arom}), 129.3 (2C, C_{arom}), 133.7 (2C, C_{arom}), 146.6 (C^4), 152.9 (C^5), 160.5 (C=O), 163.4 (C=O).

Iodosulfonation–dehydroiodination of acrylic acid derivatives (*general procedure*). An aqueous solution of sodium methanesulfinate was obtained by reduction of 17 g (150 mmol) of methanesulfonyl chloride with 20.8 g (165 mmol) of Na_2SO_3 in the presence of 25.2 g (300 mmol) of $NaHCO_3$ [40]. The solution was treated with 13 g (51 mmol) of iodine in 80 ml of benzene under stirring over a period of 40 min. The benzene layer was separated, dried over $MgSO_4$, and added to a solution of 40 mmol of methyl acrylate or acrylonitrile in 20 mL of benzene, and the mixture was placed into a Pyrex flask and irradiated for 1 h with a halogen filament lamp (500 W). The solvent was removed under reduced pressure on a rotary evaporator, the residue was treated with 100 mL of anhydrous methylene chloride, and 3 g (30 mmol) of triethylamine was added dropwise under stirring. The mixture was stirred for 2 h, the precipitate of triethyl-

amine hydroiodide was filtered off and washed on a filter with 15 mL of ethanol–petroleum ether (1:2), the filtrate was combined with the washings and evaporated, and the residue was recrystallized.

Methyl (2*E*)-3-(methanesulfonyl)prop-2-enoate (9). Yield 2.3 g (74%), mp 77–78°C. IR spectrum, ν, cm^{-1}: 1717 s, 1640 w, 1458 w, 1439 m, 1416 m, 1335 s, 1312 v.s, 1296 v.s, 1242 s, 1173 m, 1138 v.s, 999 m, 980 s, 922 m, 868 w, 799 m, 775 m, 698 w, 521 m, 509 s, 467 m. ^{1}H NMR spectrum, δ, ppm: 3.01 s (3H, Me), 3.82 s (3H, OMe), 6.84 d (1H, 2-H, J = 15.2 Hz), 7.93 d (1H, 3-H, J = 15.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 42.4 (Me), 53.0 (OMe), 132.5 (C^2), 142.2 (C^3), 163.8 (C=O). Found, %: C 36.51; H 4.90; S 19.46. $C_5H_8O_4S$. Calculated, %: C 36.58; H 4.91; S 19.53.

(2*E*)-3-(Methanesulfonyl)prop-2-enenitrile (10). Yield 1.8 g (64%), mp 103–104°C [41]. IR spectrum, ν, cm^{-1}: 3071 m, 3009 m, 2928 m, 2238 m, 1617 m, 1412 m, 1327 v.s, 1312 v.s, 1269 s, 1211 s, 1138 v.s, 972 s, 941 s, 829 s, 795 m, 752 s, 544 v.s, 521 s, 490 s, 455 m. ^{1}H NMR spectrum, δ, ppm: 3.05 s (3H, Me), 6.56 d (1H, 2-H, J = 15.8 Hz), 7.34 d (1H, 3-H, J = 15.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 42.4 (Me), 113.1 (C^2), 113.3 (CN), 147.8 (C^3).

Reaction of compounds 9 and 10 with diphenyldiazomethane (*general procedure*). A solution of 0.65 g (3.3 mmol) of diphenyldiazomethane in 10 mL of anhydrous diethyl ether was added to a solution of 3 mmol of compound **9** or **10** in 70 mL of the same solvent, and the mixture was kept for 24 h at 20°C in the dark. The crystals were filtered off and washed with diethyl ether.

Methyl 3-(methanesulfonyl)-5,5-diphenyl-4,5-dihydro-1*H*-pyrazole-4-carboxylate (11). Yield 71%, light yellow crystals, mp 179–180°C. IR spectrum, ν, cm^{-1}: 3333 s, 1748 s, 1732 s, 1543 m, 1447 m, 1431 m, 1420 m, 1296 v.s, 1235 m, 1181 m, 1161 m, 1134 s, 1115 m, 1088 w, 1026 m, 972 m, 957 m, 872 m, 772 s, 752 m, 706 m, 695 s, 613 m, 548 m, 525 s, 505 m. ^{1}H NMR spectrum, δ, ppm: 3.18 s (3H, Me), 3.20 s (3H, OMe), 5.01 s (1H, 4-H), 7.24–7.33 m (7H, H_{arom}), 7.29 s (1H, NH), 7.36–7.41 m (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 43.0 (Me), 52.5 (OMe), 58.9 (C^4), 80.7 (C^5), 126.2 (2C, C_{arom}), 128.15 (2C, C_{arom}), 128.25 (2C, C_{arom}), 128.5 (C_{arom}), 128.8 (C_{arom}), 129.2 (2C, C_{arom}), 139.1 (C_{arom}), 143.3 (C_{arom}), 146.6 (C^3), 167.8 (C=O). Found, %: C 60.28; H 4.99; N 7.72; S 9.06. $C_{18}H_{18}N_2O_4S$. Calculated, %: C 60.32; H 5.06; N 7.82; S 8.95.

3-(Methanesulfonyl)-5,5-diphenyl-4,5-dihydro-1*H*-pyrazole-4-carbonitrile (12). Yield 68%, colorless crystals, mp 71–72°C. IR spectrum, ν, cm^{-1}: 2978 m, 2928 w, 2836 w, 2242 w, 1536 m, 1497 m, 1451 m, 1431 m, 1389 w, 1370 m, 1319 v.s, 1238 w, 1196 m, 1146 s, 1103 m, 1069 m, 1019 w, 1003 w, 961 m, 772 s, 702 s, 529 s, 502 m. ^{1}H NMR spectrum, δ, ppm: 3.20 s (3H, Me), 5.07 s (1H, 4-H), 7.29 br.s (1H, NH), 7.22–7.25 m (2H, H_{arom}), 7.30–7.32 m (2H, H_{arom}), 7.39–7.42 m (6H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 43.1 (Me), 49.5 (C^4), 81.6 (C^5), 113.4 (CN), 125.9 (2C, C_{arom}), 127.5 (2C, C_{arom}), 129.1 (2C, C_{arom}), 129.4 (C_{arom}), 129.5 (2C, C_{arom}), 138.6 w (C_{arom}), 141.1 w (C_{arom}), 141.9 (C^3). Found, %: C 62.78; H 4.51; N 12.83; S 9.86. $C_{17}H_{15}N_3O_2S$. Calculated, %: C 62.75; H 4.65; N 12.91; S 9.85.

Thermal isomerization of 3*H*-pyrazoles 3c, 4c, and 4d (*general procedure*). A solution of 0.45 mmol of pyrazole **3c**, **4c**, or **4d** in 3 mL of anhydrous toluene was refluxed for 1 h under argon. The solvent was removed on a rotary evaporator, and the residue was analyzed by NMR. The products were *N*-phenyl-1*H*-pyrazoles **13c** and **13d** and 1*H*-pyrazole **15c**, respectively.

Methyl 1,5-diphenyl-1*H*-pyrazole-4-carboxylate (13c). Yield 65%, colorless crystals, mp 125–126°C [19]. IR spectrum, ν, cm^{-1}: 2948 w, 1725 v.s (C=O), 1551 m, 1497 m, 1451 m, 1389 m, 1289 m, 1223 v.s, 1130 s, 1084 m, 1019 m, 772 m, 702 m, 695 m. ^{1}H NMR spectrum, δ, ppm: 3.74 s (3H, OCH_3), 7.17–7.23 m (2H, H_{arom}), 7.24–7.38 m (8H, H_{arom}), 8.17 s (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 51.2 (OCH_3), 113.5 (C^4), 125.3 (2C, C_{arom}), 127.9 (C_{arom}), 128.0 (2C, C_{arom}), 128.8 (3C, C_{arom}), 129.1 (C_{arom}), 130.5 (2C, C_{arom}), 139.3 w (C_{arom}), 142.4 (C^5), 145.5 (C^3), 163.3 (C=O).

1,5-Diphenyl-1*H*-pyrazole-4-carbonitrile (13d). Yield 92%, colorless crystals, mp 95–96°C; published data: mp 102–104°C [20], 100°C [21]. IR spectrum, ν, cm^{-1}: 3067 w, 2230 s (CN), 1593 m, 1543 m, 1501 v.s, 1447 s, 1401 s, 1069 m, 965 m, 857 m, 772 s, 706 v.s, 695 s, 656 m. ^{1}H NMR spectrum, δ, ppm: 7.25–7.27 m (2H, H_{arom}), 7.31–7.34 m (2H, H_{arom}), 7.35–7.39 m (5H, H_{arom}), 7.40–7.42 m (1H, H_{arom}), 8.03 s (5-H). ^{13}C NMR spectrum, δ_C, ppm: 93.8 (C^4), 113.9 (CN), 125.2 (2C, C_{arom}), 126.6 w (C_{arom}), 128.7 (C_{arom}), 129.0 (2C, C_{arom}), 129.1 (2C, C_{arom}), 129.2 (2C, C_{arom}), 130.1 (C_{arom}), 138.6 w (C_{arom}), 142.8 (C^5), 147.6 (C^3).

Methyl 4,5-diphenyl-1*H*-pyrazole-3-carboxylate (15c). Yield 52%, mp 215–216°C (from MeOH);

published data [18]: mp 218°C (from MeOH). IR spectrum, ν, cm^{-1}: 3279 m, 1732 v.s, 1458 m, 1443 m, 1404 m, 1292 w, 1254 m, 1208 s, 1165 m, 1103 m, 1038 m, 1011 m, 768 m, 694 s. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.33 s (1H, NH), 3.69 s (3H, OMe), 7.21–7.23 m (2H, H_{arom}), 7.29–7.36 m (8H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 51.4 (OMe), 127.1 br (C^4), 127.5 (4C, C_{arom}), 127.9 (4C, C_{arom}), 128.4 br and 132.3 br (C^3, C^5).

Methyl 5-methyl-1,5-diphenyl-1*H*-pyrazole-4-carboxylate (20c). A solution of 58 mg (0.2 mmol) of 3*H*-pyrazole **5c** in 3 mL of anhydrous benzene was heated for 40 min at 140°C in a microwave reactor. The solution was concentrated, and the colorless crystals were filtered off. Yield 35 mg (60%), mp 129–130°C [22]. IR spectrum, ν, cm^{-1}: 1717 v.s, 1551 m, 1505 m, 1462 m, 1435 m, 1420 m, 1385 m, 1312 m, 1239 s, 1188 m, 1165 m, 1100 s, 1076 m, 768 m, 702 m, 691 m. ^1H NMR spectrum, δ, ppm: 2.59 s (3H, Me), 3.69 s (3H, OMe), 7.15–7.18 m (2H, H_{arom}), 7.23–7.27 m (5H, H_{arom}), 7.29–7.36 m (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.5 (Me), 51.5 (OMe), 111.7 (C^4), 125.4 (2C, C_{arom}), 127.8 (C_{arom}), 128.1 (2C, C_{arom}), 128.9 (2C, C_{arom}), 129.1 (C_{arom}), 129.8 (C_{arom}), 130.5 (2C, C_{arom}), 139.2 (C^3), 146.6 (C^5), 151.9 (C_{arom}), 164.4 (C=O).

Thermal transformations of 3*H*-pyrazole 7c. *a*. A solution of 0.25 g (0.75 mmol) of 3*H*-pyrazole **7c** in 15 mL of ethanol was refluxed for 40 min. The solvent was removed on a rotary evaporator. According to the NMR data, the product was compound **22** with a small impurity of indene **24** (7%). Crystallization from diethyl ether gave 0.15 g (60%) of **22**.

b. A solution of 0.5 g (1.5 mmol) of **7c** in 15 mL of anhydrous toluene was refluxed for 1 h, and the solvent was removed on a rotary evaporator. According to the ^1H NMR data, the residue was a mixture of **22** and **24** at a ratio of 1:1.3. The mixture was separated by silica gel flash chromatography using methyl *tert*-butyl ether–petroleum ether (1:4) as eluent.

Dimethyl 3,4-diphenyl-4*H*-pyrazole-4,5-dicarboxylate (22). Yield 0.129 g (25%), colorless crystals, mp 154–155°C; published data [24]: mp 150°C. UV spectrum (MeOH): λ_{max} 313 nm (log ε 4.03). IR spectrum, ν, cm^{-1}: 3071 w, 2952 w, 1755 v.s, 1717 s, 1516 m, 1497 m, 1443 s, 1350 s, 1227 s, 1196 s, 1157 s, 1007 w, 957 w, 814 w, 756 w, 691 s. ^1H NMR spectrum, δ, ppm: 3.69 s (3H, OMe), 3.87 s (3H, OMe), 7.30–7.38 m (7H, H_{arom}), 7.45–7.50 m (1H, H_{arom}), 7.96–7.98 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 53.2 (OMe), 53.9 (OMe), 77.4 (C^4), 127.8 w (C_{arom}), 128.5 (2C, C_{arom}), 129.0 (2C, C_{arom}), 129.2 (2C, C_{arom}), 129.3 (C_{arom}), 129.8 w (C_{arom}), 130.0 (2C, C_{arom}), 132.9 (C_{arom}), 160.1 (C=O), 165.6 (C=O), 168.0 (C^3), 175.4 (C^5).

Dimethyl 3-phenyl-1*H*-indene-1,2-dicarboxylate (24). Yield 0.18 g (36%), colorless crystals, mp 86–87°C; published data: mp 92–93°C (from MeOH) [26], 93–94°C (from MeOH) [27]. IR spectrum, ν, cm^{-1}: 3083 w, 3025 w, 3013 w, 2955 w, 2901 w, 1744 v.s, 1709 v.s, 1431 m, 1347 m, 1331 m, 1308 m, 1242 m, 1204 s, 1161 s, 1146 s, 1123 m, 1096 m, 1034 w, 698 m. ^1H NMR spectrum, δ, ppm: 3.66 s (3H, OMe), 3.72 s (3H, OMe), 4.84 s (1H, 1-H), 7.24–7.26 m (1H, H_{arom}), 7.32–7.48 m (7H, H_{arom}), 7.63–7.65 m (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 51.7 (OMe), 52.8 (OMe), 55.9 (C^1), 123.5 (C_{arom}), 123.9 (C_{arom}), 128.1 (2C, C_{arom}), 128.4 (C_{arom}), 128.7 (C_{arom}), 128.9 (C_{arom}), 129.0 (2C, C_{arom}), 129.7 (C^2), 133.3 (C_{arom}), 141.0 (C_{arom}), 144.3 (C_{arom}), 155.5 (C^3), 164.6 (C=O), 170.5 (C=O).

Thermal isomerization of 3*H*-pyrazoles 7b, 8a, 8b, and 8k (*general procedure*). A solution of 0.5 mmol of 3*H*-pyrazole **7b**, **8a**, **8b**, or **8k** in 10 mL of anhydrous carbon tetrachloride was refluxed for 4–5 h under argon. The solvent was removed on a rotary evaporator, and the residue was analyzed by NMR. From compound **7b** we obtained 4*H*-pyrazole **26b** which was purified by recrystallization from ethanol, the reaction with **8a** gave a mixture of **27a** and **28a** at a ratio of 1:3, pyrazole **8b** was converted into **28b**, and **8k**, into **28k**. Pyrazoles **28a**, **28b**, and **28k** were isolated as crystalline substances. Compound **27a** was characterized by spectral data in a mixture with isomer **28a**; attempted isolation of **27a** by silica gel column chromatography led to its transformation into pyrazolone **29**.

Methyl 5-(methanesulfonyl)-3,4-diphenyl-4*H*-pyrazole-4-carboxylate (26b). Yield 0.23 g (77%), mp 138–139°C (from petroleum ether). IR spectrum, ν, cm^{-1}: 1755 s, 1709 v.s, 1323 w, 1312 w, 1238 m, 1211 m, 737 m, 706 w, 694 m. ^1H NMR spectrum, δ, ppm: 3.01 s (3H, CH_3), 3.77 s (3H, OMe), 7.37–7.42 m (7H, H_{arom}), 7.52 t (1H, H_{arom}, J = 8.7 Hz), 7.96 d (2H, H_{arom}, J = 7.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 43.4 (Me), 54.3 (OMe), 77.9 (C^4), 127.1 w (C_{arom}), 128.5 w (C_{arom}), 128.7 (2C, C_{arom}), 129.5 (2C, C_{arom}), 129.96 (C_{arom}), 130.04 (2C, C_{arom}), 133.4 (C_{arom}), 164.4 (C=O), 175.3 (C^3), 175.6 (C^5). Found, %: C 60.68; H 4.47; N 7.82; S 9.06. $C_{18}H_{16}N_2O_4S$. Calculated, %: C 60.66; H 4.53; N 7.86; S 9.00.

5-(4-Methylbenzenesulfonyl]-3,4-diphenyl-4*H*-pyrazole-4-carbonitrile (27a). Yield 37%; the product contained 15% of **28a**. ^{1}H NMR spectrum, δ, ppm: 2.40 s (3H, CH_3), 7.24 t (4H, H_{arom}, J = 8.1 Hz), 7.33–7.43 m (5H, H_{arom}), 7.50 t (1H, H_{arom}, J = 7.2 Hz), 7.65 d (2H, H_{arom}, J = 8.0 Hz), 7.86 d (2H, H_{arom}, J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.7 (Me), 64.5 (C^4), 111.0 (CN), 125.4 w (C_{arom}), 125.6 w (C_{arom}), 126.0 (2C, C_{arom}), 129.0 (2C, C_{arom}), 129.1 (C_{arom}), 129.3 (2C, C_{arom}), 129.4 (2C, C_{arom}), 130.0 (2C, C_{arom}), 133.8 (C_{arom}), 134.8 w (C_{arom}), 146.5 w (C_{arom}), 173.6 and 173.8 (C^3, C^5). Found, %: C 69.18; H 4.21; N 10.49; S 8.06. $C_{23}H_{17}N_3O_2S$. Calculated, %: C 69.16; H 4.29; N 10.52; S 8.03.

3-(4-Methylbenzenesulfonyl)-1,5-diphenyl-1*H*-pyrazole-4-carbonitrile (28a). Yield 48%, colorless crystals, mp 203–204°C (from EtOH). IR spectrum, ν, cm^{-1}: 2242 w (CN), 1501 m, 1339 s (SO_2, asym.), 1157 v.s (SO_2, sym.), 1096 m, 791 m, 779 m, 706 m, 695 m, 660 m, 594 m, 536 m. ^{1}H NMR spectrum, δ, ppm: 2.46 s (3H, CH_3), 7.22–7.28 m (4H, H_{arom}), 7.34–7.46 m (8H, H_{arom}), 8.10 d (2H, H_{arom}, J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.7 (Me), 93.6 (C^4), 111.3 (CN), 125.3 (C_{arom}), 125.4 (2C, C_{arom}), 128.6 (2C, C_{arom}), 129.1 (4C, C_{arom}), 129.3 (C_{arom}), 129.6 (C_{arom}), 130.2 (2C, C_{arom}), 130.8 (C_{arom}), 136.5 w (C_{arom}), 137.6 w (C_{arom}), 145.7 w (C_{arom}), 150.3 (C^5), 154.1 (C^3). Found, %: C 69.22; H 4.39; N 10.56; S 8.11. $C_{23}H_{17}N_3O_2S$. Calculated, %: C 69.16; H 4.29; N 10.52; S 8.03.

3-(Methanesulfonyl)-1,5-diphenyl-1*H*-pyrazole-4-carbonitrile (28b). Yield 90%, colorless crystals, mp 225–226°C. IR spectrum, ν, cm^{-1}: 3021 w, 2924 w, 2238 w, 1593 w, 1497 m, 1319 v.s, 1150 m, 775 m, 714 w, 698 m. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.32 s (3H, Me), 7.41–7.56 m (10H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 43.1 (Me), 92.1 (C^4), 111.3 (CN), 125.3 (C_{arom}), 126.0 (2C, C_{arom}), 129.0 (2C, C_{arom}), 129.38 (2C, C_{arom}), 129.44 (2C, C_{arom}), 129.9 (C_{arom}), 130.8 (C_{arom}), 137.4 (C_{arom}), 150.6 (C^5), 152.2 (C^3). Found, %: C 63.17; H 4.11; N 12.87; S 10.05. $C_{17}H_{13}N_3O_2S$. Calculated, %: C 63.14; H 4.05; N 12.99; S 9.91.

3-(Benzenesulfonyl)-1,5-diphenyl-1*H*-pyrazole-4-carbonitrile (28k). Yield 82%, colorless crystals, mp 219–220°C. IR spectrum, ν, cm^{-1}: 2253 w, 1501 m, 1447 m, 1343 s, 1204 w, 1157 v.s, 1123 w, 1096 m, 791 m, 783 m, 748 m, 733 m, 706 m, 694 m, 683 m, 629 s, 598 m, 559 m, 540 m. ^{1}H NMR spectrum, δ, ppm: 7.20–7.29 m (4H, H_{arom}), 7.32–7.41 m (5H, H_{arom}), 7.41–7.47 m (1H, H_{arom}), 7.62 t (2H, H_{arom}, J = 7.9 Hz), 7.70 t (1H, H_{arom}, J = 7.4 Hz), 8.22 d (2H, H_{arom}, J = 7.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 94.0 (C^4), 111.4 (CN), 125.4 (C_{arom}), 125.6 (2C, C_{arom}), 128.8 (2C, C_{arom}), 129.3 (4C, C_{arom}), 129.5 (2C, C_{arom}), 129.7 (2C, C_{arom}), 131.1 (C_{arom}), 134.6 (C_{arom}), 137.8 w (C_{arom}), 139.6 w (C_{arom}), 150.3 (C^5), 154.0 (C^3). Found, %: C 68.47; H 4.00; N 10.82; S 8.30. $C_{22}H_{15}N_3O_2S$. Calculated, %: C 68.56; H 3.92; N 10.90; S 8.32.

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