ISSN 1070-4280, Russian Journal of Organic Chemistry, 2018, Vol. 54, No. 6, pp. 892–900. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © V.A. Vasin, V.V. Razin, E.V. Bezrukova, Yu.A. Popkova, N.V. Somov, 2018, published in Zhurnal Organicheskoi Khimii, 2018, Vol. 54, No. 6, pp. 890–897.

Rearrangements of 3*H*-Pyrazoles—Adducts of Dimethyl Acetylenedicarboxylate with Diphenyldiazomethane and 9-Diazofluorene

V. A. Vasin[†a], V. V. Razin[b], E. V. Bezrukova[a],* Yu. A. Popkova[a], and N. V. Somov[c]

[a] *Ogarev Mordovian State University, ul. Bol'shevistskaya 68, Saransk, 430005 Russia*
**e-mail: tadaakiyattsu@gmail.com*

[b] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*

[c] *Lobachevskii Nizhny Novgorod State University, pr. Gagarina 23, Nizhny Novgorod, 603950 Russia*

Received June 14, 2017

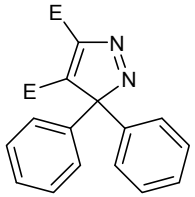
Abstract—Structurally related 3*H*-pyrazoles resulting from 1,3-dipolar cycloaddition of diphenyldiazomethane and 9-diazofluorene to dimethyl acetylenedicarboxylate undergo van Alphen–Hüttel rearrangement on heating in a polar solvent (methanol, ethanol, acetic acid). In the first case, the rearrangement involves strictly regioselective 1,5-phenyl migration toward the carbon atom with the formation of relatively stable 4*H*-pyrazole. Post-rearrangement of the product on heating at 180°C in toluene gives a mixture of methyl 1*H*-pyrazole-1-carboxylates via successive migrations of the CO_2Me group. In the second case, the aryl substituent concurrently migrates both to nitrogen atom with the formation of 1*H*-pyrazole structure (phenanthridine derivative) and to carbon atom with subsequent rearrangement of unstable 4*H*-pyrazole to 3*H*-pyrazole fused to phenanthrene fragment. Heating of dimethyl acetylenedicarboxylate adducts (3*H*-pyrazoles) in an aprotic solvent (benzene, toluene) leads to the corresponding denitrogenation products. This process is especially facile for the spirocyclic 3*H*-pyrazole derived from 9-diazofluorene, and it yields cyclopropene derivative. Some previous errors in the structure determination of the rearrangement products have been corrected.

DOI: 10.1134/S1070428018060118

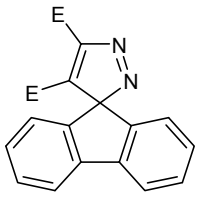
Two structurally related compounds **1** and **2** synthesized via 1,3-dipolar cycloaddition of diphenyldiazomethane and 9-diazofluorene to dimethyl acetylenedicarboxylate [1, 2] have become the first and important subjects of studies which have led to the discovery of thermal transformations of 3*H*-pyrazoles currently known as van Alphen–Hüttel rearrangement [3]. Interest in such transformations of 3*H*-pyrazoles persists so far, and more complete interpretation of the Alphen–Hüttel rearrangement has been proposed [4–7]. Furthermore, its useful applications for organic synthesis have been revealed [6–8].

In keeping with the modern concepts, the van Alphen–Hüttel rearrangement of 3,3-disubstituted 3*H*-pyrazoles is considered as 1,5-sigmatropic shift of substituent from the 3-position. The 3-substituent is capable of migrating in two directions, with the formation of *N*-substituted 1*H*-pyrazole derivative or 4*H*-pyrazole; in some cases, the rearrangement in one or another direction was highly regioselective [8, 9].

Seemingly, the results of rearrangement of compounds **1** and **2** have been determined long ago and are reliable. However, our recent studies on the isomerization of structurally related 3*H*-pyrazoles [10–12] prompted us to revise the results of thermal transformations of pyrazoles **1** and **2**. One of the reasons was recently increased interest in so-called van Alphen–Hüttel post-rearrangement. This process involves further transformations of one product of the



1



2

[†] Deceased.

Hereinafter, E = CO_2Me.

isomerization of 3*H*-pyrazole, 4*H*-pyrazole derivative. Completely substituted 3*H*-pyrazole and 4*H*-pyrazole are isomeric conjugated systems, so that a rearrangement analogous to the rearrangement of 3*H*-pyrazole may be quite admissible for 4-*H*-pyrazole. However, available data on thermal transformations of 4*H*-pyrazoles are incommensurably poorer than the data on analogous transformations of 3*H*-pyrazoles [9, 13].

The results of thermolysis of pyrazole **1** [1] were rechecked for the first time by Baumes et al. [14]. It was shown experimentally that 4*H*-pyrazole **3** is the only product of the reaction in glacial acetic acid at 100°C. The authors revealed that van Alphen erroneously assigned the 1*H*-pyrazole structure **4** to the product of thermolysis of compound **1**. The data given in [15], which seemingly confirmed van Alphen's conclusions, were in fact erroneous, as we reported in [12].

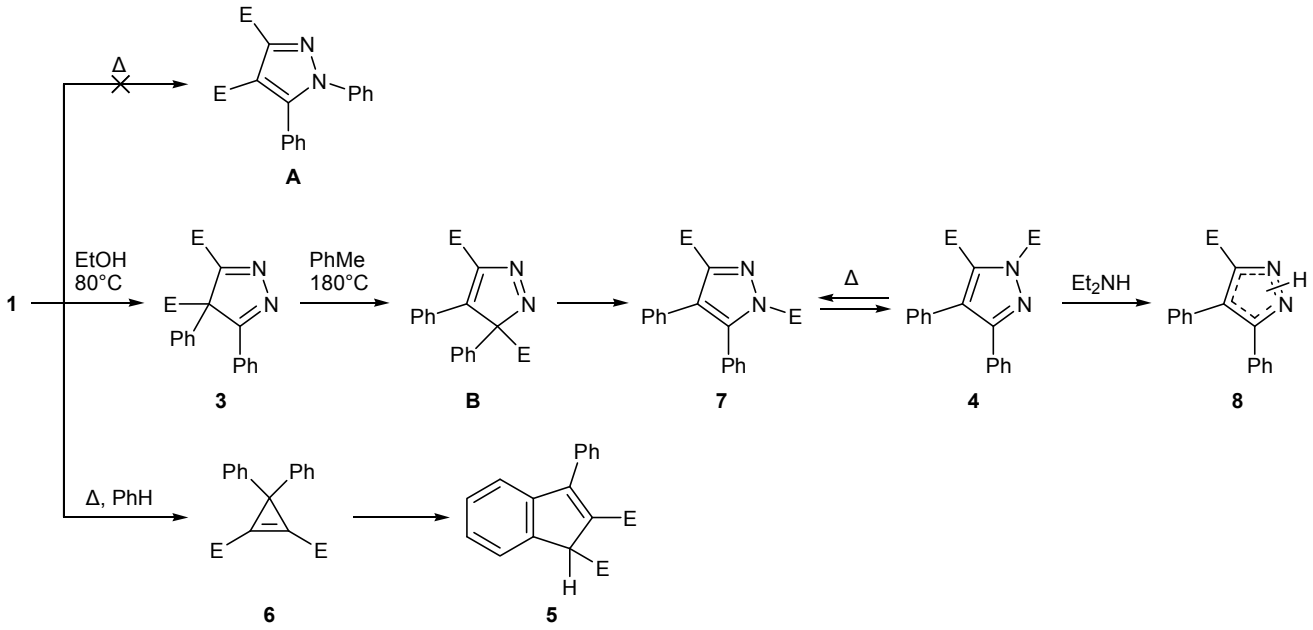
The results of [14] have aroused a keen interest in the van Alphen–Hüttel rearrangement, and the formation of 4*H*-pyrazole derivatives, often together with *N*-substituted 1*H*-pyrazoles, in the thermolysis of other 3*H*-pyrazoles was confirmed in a number of publications [16–33]. More recent studies on this topic were reviewed in [8, 9] and reported in [34–41].

We reproduced the experiment described in [14] and, in fact, obtained 4*H*-pyrazole **3** as the only product on heating compound **1** in acetic acid (Scheme 1). In our previous study [12], the thermolysis of 3*H*-pyrazole **1** in boiling toluene afforded compound **3** in a mixture with a comparable amount of indene **5**. When the thermolysis was carried out in ethanol, the amount of **5** was insignificant.

Taking into account that indene **5** (together with isomeric cyclopropene derivative **6**) can be synthesized by photolysis of 3*H*-pyrazole **1** [42, 43], we reproduced the described procedure. By varying the temperature, we found conditions under which not only compounds **3** and **5** but also cyclopropene **6** were detected by ^{13}C NMR among the thermolysis products of pyrazole **1** in benzene (~65–70°C). Special experiment showed that cyclopropene **6** is quantitatively converted to indene **5** on heating in boiling toluene. No other thermolysis products, including hypothetical *N*-phenyl-1*H*-pyrazole **A** (product of phenyl group migration to nitrogen), were detected. We were the first to observe thermal fragmentation of compound **1**, though analogous fragmentation accompanying van Alphen–Hüttel rearrangement of other 3,3-diphenyl-3*H*-pyrazoles was described previously [25, 28, 34, 41]. Thermal 3-phenylcyclopropene–indene isomerization is also well known [34, 44–46].

We then studied for the first time high-temperature transformations of 4*H*-pyrazole **3**. This compound turned out to be considerably more stable than 3*H*-pyrazole **1**. The complete conversion of **3** was achieved only on heating in toluene at 180°C in a microwave furnace, and a mixture of *N*-methoxycarbonyl-1*H*-pyrazoles **4** and **7** was formed; after heating in boiling *p*-xylene for 10 h, the conversion of pyrazole **3** did not exceed 12%.

Scheme 1.



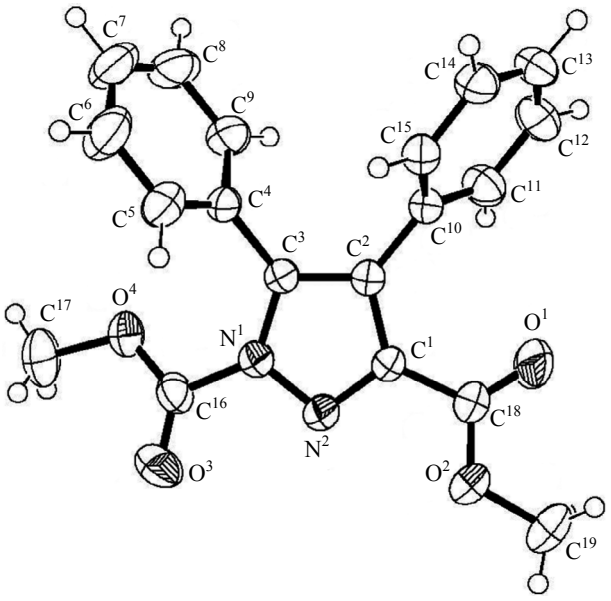


Fig. 1. Structure of the molecule of dimethyl 4,5-diphenyl-1*H*-pyrazole-1,3-dicarboxylate (**7**) according to the X-ray diffraction data.

Pure compounds **4** and **7** were isolated from their mixture by flash chromatography on silica gel. Compound **7** was a crystalline solid, and isomer **4** was liquid under normal conditions. Their structure was confirmed by IR and ^{1}H and ^{13}C NMR spectra. The structure of **7** was unambiguously determined by X-ray analysis of its single crystal (Table 1, Fig. 1). Compounds **4** and **7** can be regarded as carbamate derivatives; they are relatively readily converted to known 1*H*-pyrazole **8** [12] by keeping at 20°C in diethyl ether solution containing a small excess of diethylamine [6].

To rationalize the results of thermal isomerization of 4*H*-pyrazole **3**, we presumed that the methoxycarbonyl group, being more labile than phenyl substituent [6], migrates from the 4-position to C^5 rather than C^3 (1,5-sigmatropic shift) with the formation of 3*H*-pyrazole **B**. By analogy with the isomerization of related 3*H*-pyrazoles [12], the observed regioselectivity in the migration of the CO_2Me group is likely to be determined by the directing effect of the other ester group on C^3 [36]. We failed to detect presumed intermediate **B**.

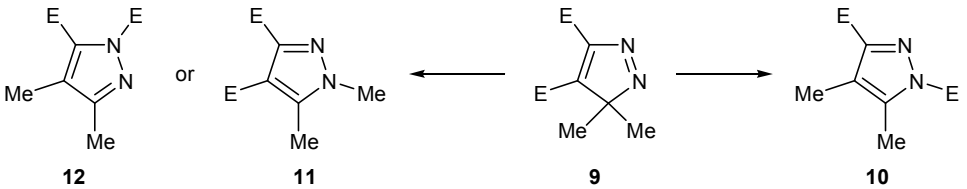
1*H*-Pyrazole **7** in toluene at 180°C was largely converted to isomer **4**. Under the same conditions, only ≤10% of pure 1*H*-pyrazole **4** isomerized to **7**. Thus, 1*H*-pyrazoles **4** and **7** are thermally interconvertible via 1,5-sigmatropic rearrangement [47]. We believe that the primary isomerization product of 4*H*-pyrazole **3** is 1*H*-pyrazole **7** which is transformed to more stable isomer **4** under thermolysis conditions.

Frampton et al. [36] reported two products of thermolysis of compound **9** (3,3-dimethyl analog of **1**) in benzene at 160°C. The major product was 1*H*-pyrazole **10** (an analog of **7**) whose structure was reliably proved by X-ray analysis. The other product was assigned the structure of *N*-methyl-1*H*-pyrazole **11**, though, in our opinion, there were no sufficient grounds for this assignment. We believe that the second product was in fact compound **12**, an analog of **4** (Scheme 2).

Thus, van Alphen [1] erroneously assigned the structure of the thermolysis product of 3*H*-pyrazole **1** on the basis of indirect evidences, namely easy fragmentation of 1*H*-pyrazole **4** to monoester **8** by the action of concentrated sulfuric acid [1]; as follows from our results, analogous fragmentation of 4*H*-pyrazole **3** is also possible.

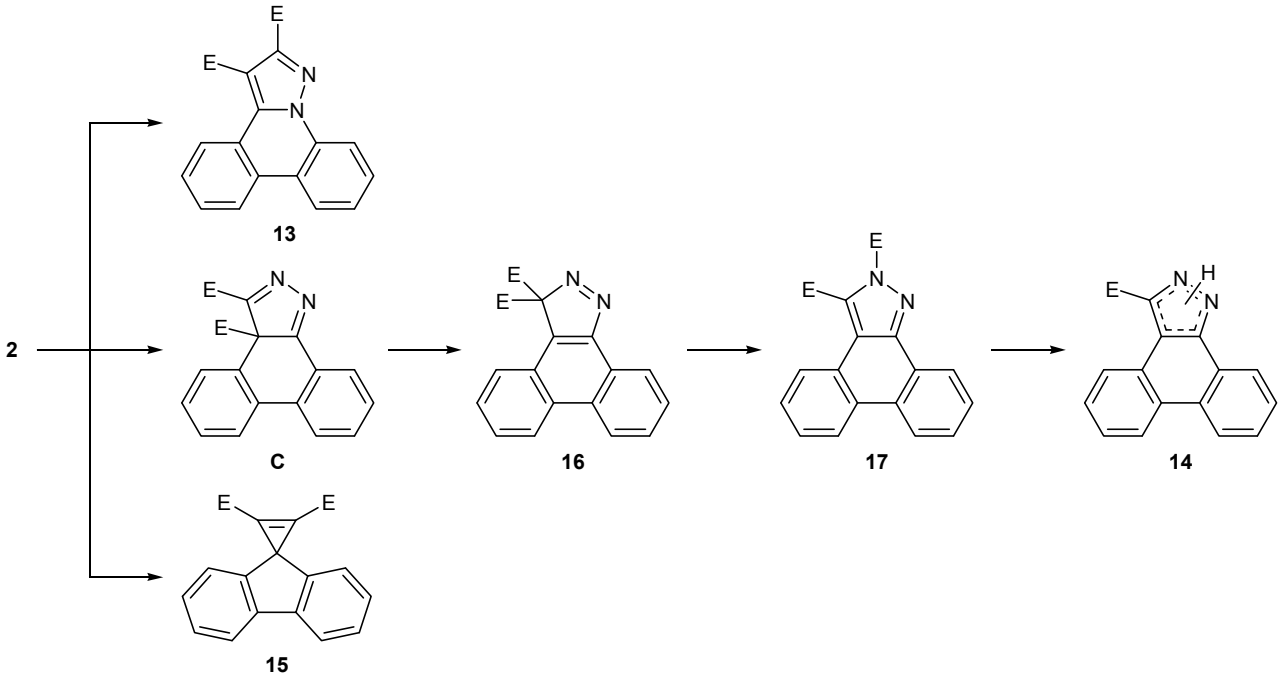
Now let us proceed with a spirocyclic analog of 3*H*-pyrazole **1**, compound **2**. According to van Alphen [2], 3*H*-pyrazole **2** in acetic acid at 100°C is converted to 1*H*-pyrazole **13**, and fragmentation of **2** on treatment with hot concentrated sulfuric acid gives 1*H*-pyrazole **14** (Scheme 3). It was also noted that compound **14** is not formed from **13**. Reimlinger [48] later reported that heating of 3*H*-pyrazole **2** in boiling benzene leads only to denitrogenation with the formation of cyclopropene **15**. Mataka and Tashiro [32] determined the composition of the thermolysis products of compound **2** in different solvents (methanol, ethanol, acetonitrile, benzene, toluene). Cyclopropene derivative **15** was formed in an aprotic nonpolar solvent (benzene or toluene), which confirmed the data of [48]. However, the thermolysis of **2** in polar solvents gave compound **15** and three other nitrogen-containing compounds which were identified as 3*H*-pyrazole **16** and 1*H*-pyrazoles **14** and **17**.

Scheme 2.



12 **11** **9** **10**

Scheme 3.



We studied the thermolysis of **2** in acetic acid, as well as its transformation in glacial acetic acid at 20°C in the presence of a catalytic amount of concentrated sulfuric acid. In the first case, we obtained three products, compounds **13**, **14**, and **17**. Poorly soluble indazole **14** was separated by filtration (yield 29%), and the filtrate contained (according to the ^{1}H NMR data) compounds **13** and **17** at a ratio of 3:1, which were difficult to separate. In the second case, the only product was indazole **14** which was likely to be formed as a result of hydrolysis of **17** during the isolation procedure. Indazole **14** was also reported as the only product of thermolysis of **2** in acetic acid at 100°C [20]. The structure of **14** was confirmed by spectral data.

When 3*H*-pyrazole **2** was heated in boiling methanol, a mixture of four compounds was formed. Indazole **14** precipitated from the reaction mixture and was separated by filtration (yield 32%). According to the ^{13}C NMR data, the filtrate contained cyclopropene derivative **15** identical to a sample obtained by thermolysis in benzene. The remaining two products were isolated in the pure state by flash chromatography. One of them was 3*H*-pyrazole **16** (in agreement with the data of [32]), and the second had the melting point and ^{1}H and ^{13}C NMR spectra coinciding with those given in [32] for compound **17**; however, in fact, it was 1*H*-pyrazole **13** whose structure was determined by X-ray analysis of its single crystal (Table 1, Fig. 2).

The structure of 3*H*-pyrazole **16** was confirmed by spectral data which were consistent with the data of [32]. Unfortunately, we failed to isolate pure 1*H*-pyrazole **17** by chromatographic separation of its mixture with **13** because of isomerization to **14**. Therefore, the ^{1}H and ^{13}C NMR spectra of **17** were obtained by exclusion of signals belonging to **13** from the spectra of their mixture (ratio **17**:**13** 1:3).

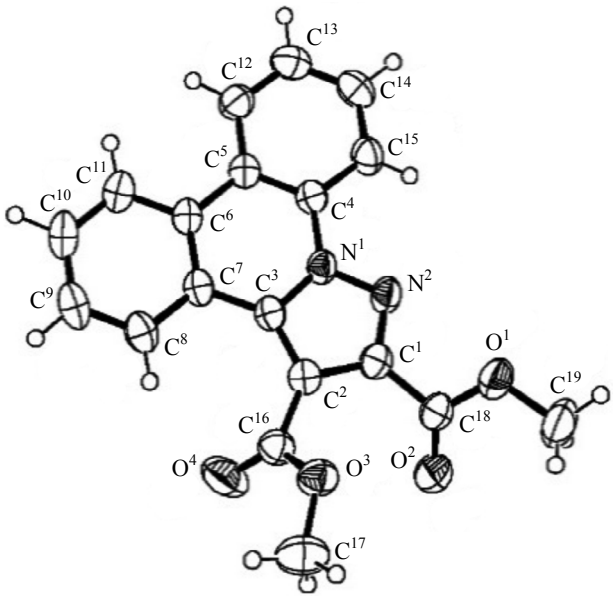
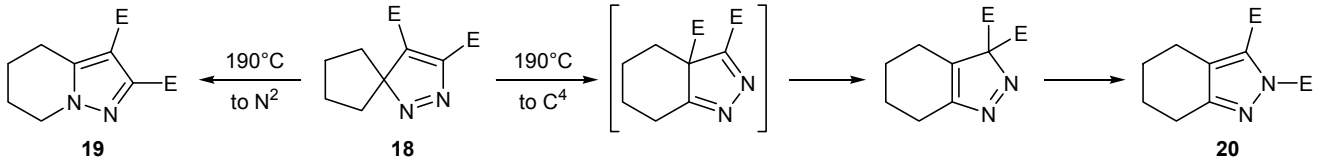


Fig. 2. Structure of the molecule of dimethyl pyrazolo[1,5-*f*]-phenanthridine-2,3-dicarboxylate (**13**) according to the X-ray diffraction data.

Scheme 4.

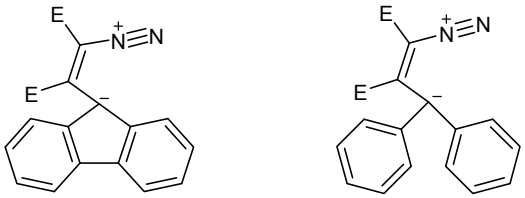


19 **18** **20**

Thus, unlike compound **1**, the van Alphen–Hüttel rearrangement of 3*H*-pyrazole **2** follows two alternative paths. 1,5-Sigmatropic shift toward the N^2 atom gives thermally stable phenanthridine derivative **13**, whereas the shift toward C^4 leads to the formation of thermally unstable 4*H*-pyrazole **C** which undergoes post-rearrangement via 1,5-migration of the methoxycarbonyl group, yielding new 3*H*-pyrazole **16**. Presumably, apart from the high mobility of the CO_2Me group, the low thermal stability of 4*H*-pyrazole **C** and its fast rearrangement to 3*H*-pyrazole **16** are determined by stabilizing effect due to formation of aromatic phenanthrene system. Compound **16** undergoes partial fragmentation to monoester **14**, seemingly through 1*H*-pyrazole **17** which is unstable in boiling methanol.

According to [40], the thermolysis of bicyclic 3*H*-pyrazole **18** (an analog of **2**) in benzene at 190°C (60 min) leads to the formation of compounds **19** and **20** (Scheme 4) which are analogous to **13** and **17**.

The pronounced tendency to fragmentation of 3*H*-pyrazole **2** during the thermolysis in benzene (in comparison to pyrazole **1**) may be explained by the greater stability of diazo compound **D** which mediates the denitrogenation process [29] due to the presence of 9-fluorenyl anion fragment (cf. structure **E** derived from **1**). No cyclopropene derivatives were detected in the thermolysis of 3*H*-pyrazole **18** and 3,3-dialkyl analogs of **1** [36], for which the corresponding denitrogenation intermediates are less stable than not only structure **D** but also **E**.



D **E**

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Jeol JNM-ECX400 spectrometer at 400.1 and 100.6 MHz, respectively, using $CDCl_3$ as solvent and reference ($CHCl_3$, δ 7.26 ppm; $CDCl_3$, δ_C 77.16 ppm). The IR spectra were recorded in KBr on an InfraLYuM FT-02 spectrometer with Fourier transform. The elemental analyses were obtained with a Vario MICRO CHNS analyzer. Sorbfil plates were used for analytical TLC (light petroleum ether–acetone, 4:1); spots were visualized by treatment with iodine vapor. Flash chromatography was performed on Merck 60 silica gel (0.040–0.063 mm); eluent light petroleum ether–acetone, 7:1 to 3:1. Dimethyl acetylenedicarboxylate was commercial product (from Aldrich).

Thermolysis of 3*H*-pyrazole 1 in benzene. A solution of 0.5 g (1.5 mmol) of 3*H*-pyrazole **1** [12] in 12 mL of anhydrous benzene was refluxed for 1 h. A mixture of 4*H*-pyrazole **3** and indene **5** at a ratio of 1.6:1 was formed. By flash chromatography on silica gel (petroleum ether–ethyl acetate, 4:1) we isolated 0.29 g (58%) of **3** and 0.18 g (36%) of **5**. The melting points and ^1H and ^{13}C NMR spectra of the isolated compounds coincided with those given in [12].

By heating 3*H*-pyrazole **1** in benzene at 65–70°C for 1 h we obtained a mixture of compounds **1**, **3**, **5**, and **6** at a ratio of 0.5:1.8:1:0.3.

Thermolysis of 3*H*-pyrazole 1 in acetic acid. A solution of 0.3 g (0.9 mmol) of 3*H*-pyrazole **1** in 8 mL of glacial acetic acid was heated for 1 h at 100°C. The mixture was cooled, diluted with 10 mL of water, and extracted with diethyl ether (3×15 mL). The extract was washed with an aqueous solution of sodium hydrogen carbonate and water and dried over $MgSO_4$, and the solvent was removed on a rotary evaporator to isolate 0.19 g (63%) of 4*H*-pyrazole **3**.

Thermal isomerization of cyclopropene derivative 6. A solution of 0.1 g (0.3 mmol) of compound **6** [43] in 10 mL of anhydrous toluene was refluxed for 3 h (until the initial compound disappeared according to the TLC data). Crystallization from light petroleum ether gave 84 mg (84%) of **5**.

Thermolysis of 4*H*-pyrazole (3). A solution of 0.1 g (0.3 mmol) of 4*H*-pyrazole **3** in 4 mL of anhydrous toluene was heated for 2 h at 180°C in a microwave reactor. The solvent was removed under reduced pressure, and the residue was a mixture of 1*H*-pyra-

zoles **4** and **7** at a ratio of 2:1 (according to the ^{1}H NMR data). The product mixture was separated by flash chromatography on silica gel.

Dimethyl 3,4-diphenyl-1*H*-pyrazole-1,5-dicarboxylate (4). Yield 59 mg (60%), colorless oily material. IR spectrum, ν, cm^{-1}: 1763 v.s (C=O), 1740 v.s (C=O), 1466 v.s, 1447 s, 1350 v.s, 1320 s, 1269 s, 1219 v.s, 1181 m, 1065 s, 980 m, 965 m, 760 m, 698 s. ^{1}H NMR spectrum, δ, ppm: 3.84 s (3H, OMe), 4.04 s (3H, OMe), 7.24–7.27 m (3H, H_{arom}), 7.28–7.33 m (5H, H_{arom}), 7.40–7.43 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 53.4 (OMe), 55.6 (OMe), 124.4 (C^4), 128.41 (CH_{arom}), 128.44 (2C, C_{arom}), 128.6 (2C, C_{arom}), 128.8 (2C, C_{arom}), 129.2 (CH_{arom}), 129.6 (C_{arom}), 129.7 (2C, C_{arom}), 130.8 (C_{arom}), 135.6 (C^3), 149.7 (C^5), 153.8 (C=O), 161.8 (C=O). Found, %: C 67.97; H 4.71; N 8.42. $C_{19}H_{16}N_2O_4$. Calculated, %: C 67.85; H 4.79; N 8.33.

Dimethyl 4,5-diphenyl-1*H*-pyrazol-1,3-dicarboxylate (7). Yield 32 mg (30%), colorless crystals, mp 194–195°C (from diethyl ether). IR spectrum, ν, cm^{-1}: 1775 v.s (C=O), 1732 v.s (C=O), 1466 m, 1447 m, 1435 m, 1343 m, 1308 v.s, 1204 s, 1173 m, 1142 m, 992 m, 845 m, 768 m, 706 m. ^{1}H NMR spectrum, δ, ppm: 3.88 s (3H, OMe), 3.98 s (3H, OMe), 7.13–7.15 m (2H, H_{arom}), 7.19–7.24 m (5H, H_{arom}), 7.29–7.35 m (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 52.5 (OMe), 55.4 (OMe), 126.8 (C^4), 127.8 (CH_{arom}), 127.9 (2C, C_{arom}), 128.1 (2C, C_{arom}), 129.05 (C_{arom}), 129.14 (CH_{arom}), 129.9 (C_{arom}), 130.0 (2C, C_{arom}), 130.4 (2C, C_{arom}), 144.01 (C^3), 145.4 (C^5), 149.8 (C=O), 162.0 (C=O). Found, %: C 67.89; H 4.88; N 8.27. $C_{19}H_{16}N_2O_4$. Calculated, %: C 67.85; H 4.79; N 8.33.

Mutual transformations of 1*H*-pyrazoles 4 and 7. *a*. A solution of 50 mg (0.15 mmol) of 1*H*-pyrazole **4** in 4 mL of anhydrous toluene was heated at 180°C for 30 min. The product was a mixture of compounds **4** and **7** at a ratio of 9:1.

b. A solution of 50 mg (0.15 mmol) of 1*H*-pyrazole **7** in 4 mL of anhydrous toluene was heated at 180°C for 40 min. The solvent was removed. According to the ^{1}H NMR data, the residue contained 1*H*-pyrazoles **4** and **7** at a ratio of 35:65.

Reaction of 1*H*-pyrazoles 4 and 7 with diethylamine. A mixture of 1*H*-pyrazoles **4** and **7** (1.8:1), 0.1 g (0.3 mmol), and 67 mg (0.9 mmol) of diethylamine in 5 mL of anhydrous diethyl ether was stirred at 20°C for 20 h. Volatile components were removed under reduced pressure (water-jet pump) to isolate 63 mg (77%) of 1*H*-pyrazole **8** as colorless crystals.

Table 1. Crystallographic data, parameters of X-ray diffraction experiments, and structure refinement parameters for compounds **7** and **13**

Parameter	**7**	**13**
Formula	$C_{19}H_{16}N_2O_4$	$C_{19}H_{14}N_2O_4$
Molecular weight	336.34	334.32
Appearance	Prisms	Needles
Crystal dimensions, mm	0.238×0.151×0.115	0.514×0.334×0.152
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Temperature, K	297(2)	297(2)
Z	2	4
a, Å	9.6641(4)	12.653(3)
b, Å	10.3573(4)	7.2325(5)
c, Å	10.5328(5)	23.507(4)
α, deg	117.634(4)	90
β, deg	110.058(4)	132.96(3)
g, deg	94.538(3)	90
V, Å^3	840.65(7)	1574.2(7)
d_{calc}, g/cm^3	1.329	1.411
μ, mm^{-1}	0.095	0.101
Correction for absorption, T_{min}/T_{max}	Multiscan [55], 0.82336/1	Multiscan [55], 0.451/1
F(000)	352	696
Range of θ, deg	2.31–30.506	3.573–30.739
Reflection indices	$-13 \le h \le 13$ $-14 \le k \le 14$ $-15 \le l \le 15$	$-16 \le h \le 16$ $-9 \le k \le 9$ $-31 \le l \le 31$
Total number of reflections	32735	55024
Number of independent reflections	5110	3908
Number of reflections with $I > 2\sigma(I)$	3568	2960
R_{int}	0.0385	0.0597
Number of variables	290	260
Goodness of fit	1.069	1.025
R [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0494$ $wR_2 = 0.1399$	$R_1 = 0.0457$ $wR_2 = 0.1124$
R (all reflections)	$R_1 = 0.0745$ $wR_2 = 0.1509$	$R_1 = 0.0628$ $wR_2 = 0.1206$
Residual electron density (min/max), $\bar{e}$/Å^3	–0.235/0.299	–0.175/0.22
Software	SHELX2014 [50], WINGX [51], CrysAlisPro [52]	

The melting point and NMR spectra of **8** coincided with those reported in [12].

Dimethyl spiro[fluorene-9,3′-pyrazole]-4′,5′-dicarboxylate (2) was synthesized according to the procedure described in [2]. Yield 86%, mp 124–125°C; published data [2]: mp 110°C (decomp.). IR spectrum, ν, cm^{-1}: 1740 v.s (C=O), 1628 m, 1451 m, 1339 m, 1273 s, 1142 m, 1107 m, 995 m, 822 m, 756 m. ^1H NMR spectrum, δ, ppm: 3.56 (OMe), 4.08 (OMe), 6.82 d (2H, H_{arom}, J = 7.6 Hz), 7.26 t (2H, H_{arom}, J = 7.5 Hz), 7.48 t (2H, H_{arom}, J = 7.4 Hz), 7.81 d (2H, H_{arom}, J = 7.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 53.13 (OMe), 53.36 (OMe), 109.8 (C^3), 121.2 (2C, CH_{arom}), 123.9 (2C, CH_{arom}), 128.5 (2C, CH_{arom}), 130.6 (2C, CH_{arom}), 132.7 (2C, C_{arom}), 143.7 (2C, C_{arom}), 148.57 (C_{arom}), 148.72 (C_{arom}), 160.3 (C=O), 161.8 (C=O).

Dimethyl spiro[cycloprop-2-ene-1,9′-fluorene]-2,3-dicarboxylate (15) was synthesized according to [32] by heating 0.4 g (1.2 mmol) of 3*H*-pyrazole **2** in 15 mL of benzene for 1 h under reflux. The product was isolated by crystallization from methanol. Yield 0.27 g (74%), yellowish crystals, mp 150–151°C; published data: mp 151–154°C (from EtOH) [48]; 146°C [49]. IR spectrum, ν, cm^{-1}: 1855 w (C=C, cyclopropene), 1732 v.s (C=O), 1435 m, 1265 s, 1130 w. ^1H NMR spectrum, δ, ppm: 3.72 s (6H, OMe), 7.27 d (2H, H_{arom}, J = 7.6 Hz), 7.34 t (2H, H_{arom}, J = 7.4 Hz), 7.44 t (2H, H_{arom}, J = 7.4 Hz), 7.84 d (2H, H_{arom}, J = 7.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 44.2 ($C^{3'}$), 53.3 (2C, OMe), 120.3 (2C, CH_{arom}), 121.0 (2C, C_{arom}), 121.5 (2C, CH_{arom}), 127.2 (2C, CH_{arom}), 128.1 (2C, CH_{arom}), 140.6 (2C, C_{arom}), 144.4 (C^2=C^3), 158.2 (2C, C=O).

Thermolysis of 3*H*-pyrazole 2 in methanol. A solution of 0.5 g (1.5 mmol) of 3*H*-pyrazole **2** in 20 mL of methanol was refluxed for 3 h. The precipitate of 1*H*-pyrazole **14** was filtered off, the filtrate was diluted with 20 mL of diethyl ether, and the precipitate of phenanthridine **13** was filtered off. The residue was subjected to flash chromatography on silica gel to isolate pure indazole **15**.

In an analytical experiment, the reaction mixture obtained after thermolysis was evaporated under reduced pressure (water-jet pump). According to the ^1H NMR data, the residue contained compounds **13**–**16** at a ratio of 1.27:0.3:1:1.33.

Dimethyl pyrazolo[1,5-*f*]phenanthridine-2,3-dicarboxylate (13). Yield 0.21 g (41%), colorless crystals, mp 153–154°C (from MeOH). IR spectrum, ν, cm^{-1}: 1724 s (C=O), 1543 m, 1447 m, 1277 m, 1219 v.s, 1142 m, 1069 m, 760 s. ^1H NMR spectrum, δ, ppm: 4.04 s (3H, OMe), 4.05 (3H, OMe), 7.49–7.56 m (2H, H_{arom}), 7.61 br.t (2H, H_{arom}, J = 7.8 Hz), 8.28–8.31 m (2H, H_{arom}), 8.46 d (1H, H_{arom}, J = 8.0 Hz), 8.61 d (1H, H_{arom}, J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 52.9 (OCH_3), 53.0 (OCH_3), 110.4, 117.4 (CH_{arom}), 122.0, 122.6, 122.8 (CH_{arom}), 123.3 (CH_{arom}), 125.7 (CH_{arom}), 126.8 (CH_{arom}), 127.7, 128.6 (CH_{arom}), 129.6 (CH_{arom}), 129.8 (CH_{arom}), 132.7, 136.2, 143.7, 162.8 (C=O), 165.5 (C=O). Found, %: C 58.39; H 4.34; N 8.31. $C_{19}H_{14}N_2O_4$. Calculated, %: C 68.26; H 4.22; N 8.38.

Methyl 1(2)*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (14). Yield 0.13 g (32%), colorless crystals, mp 294–295°C; published data: mp 298°C [2], 297–298°C [20]. IR spectrum, ν, cm^{-1}: 3191 w.br (NH), 1717 v.s (C=O), 1439 w, 1277 w, 1134 m, 1088 w, 1015 w, 810 w, 760 s, 725 w. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.01 s (3H, OMe), 7.59 t (1H, H_{arom}, J = 7.1 Hz), 7.61–7.74 m (3H, H_{arom}), 8.57 d (1H, H_{arom}, J = 7.5 Hz), 8.72 br.t (2H, H_{arom}, J = 6.6 Hz), 9.36 d (1H, H_{arom}, J = 8.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 51.95 (OMe), 115.7 (C_{arom}), 121.4 br.s (C_{arom}), 122.2 (CH_{arom}), 123.6 (CH_{arom}), 123.8 (CH_{arom}), 126.00 (C_{arom}), 126.02 (CH_{arom}), 126.4 (CH_{arom}), 127.3 (CH_{arom}), 127.5 (CH_{arom}), 127.7 (CH_{arom}), 128.2 (C_{arom}), 129.6 (C_{arom}), 135.7 br.s (C_{arom}), 139.5 br.s (C_{arom}), 163.4 (C=O). Found, %: C 73.77; H 4.47; N 10.01. $C_{17}H_{12}N_2O_2$. Calculated, %: C 73.90; H 4.38; N 10.14.

Dimethyl 3*H*-dibenzo[*e*,*g*]indazole-3,3-dicarboxylate (16). Yield 50 mg (10%), colorless crystals, mp 174–175°C; published data [32]: mp 168–169°C. IR spectrum, ν, cm^{-1}: 1763 v.s, 1451 m, 1439 m, 1258 s, 1235 v.s, 1053 s, 752 m, 721 m. ^1H NMR spectrum, δ, ppm: 3.81 s (6H, OCH_3), 7.73 t (1H, H_{arom}, J = 7.1 Hz), 7.79–7.89 m (3H, H_{arom}), 8.34 d (1H, H_{arom}, J = 8.2 Hz), 8.76–8.80 m (2H, H_{arom}), 9.09–9.13 m (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 54.3 (2C, OCH_3), 104.5 (C^3), 123.4 (CH), 123.8 (CH_{arom}), 124.5, 124.7 (CH_{arom}), 126.3, 128.2 (CH_{arom}), 128.4 (CH_{arom}), 128.8 (2C, CH_{arom}), 129.1 (CH_{arom}), 132.0, 132.52 (C_{arom}), 132.54 (C_{arom}), 153.9, 163.2 (2C, C=O). Found, %: C 68.39; H 4.37; N 8.26. $C_{19}H_{14}N_2O_4$. Calculated, %: C 68.26; H 4.22; N 8.38.

Thermolysis of 3*H*-pyrazole 2 in acetic acid. A solution of 0.5 g (1.5 mmol) of 3*H*-pyrazole **2** in 15 mL of glacial acetic acid was heated for 2 h at 100°C. After cooling, the precipitate was filtered off, washed with water, and dried under reduced pressure; we thus isolated 145 mg (29%) of **14**. The filtrate was

diluted with 15 mL of water and extracted with diethyl ether (3×15 mL), the extract was dried over $MgSO_4$, and the solvent was evaporated. According to the ^{1}H NMR data, the residue contained compounds **13** and **17** at a ratio of 1:3.

Dimethyl 2*H*-dibenzo[*e*,*g*]indazole-2,3-dicarboxylate (17) was characterized by spectral data for its mixture with **13**, since attempted isolation of this compound by chromatography resulted in its hydrolysis. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.10 s (3H, OCH_3), 4.14 s (3H, OCH_3). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 53.8 (OCH_3), 55.5 (OCH_3), 116.1, 123.1 (CH_{arom}), 123.4, 123.6 (CH_{arom}), 123.9 (CH_{arom}), 124.2 (CH_{arom}), 124.3 (CH_{arom}), 127.2, 127.4 (CH_{arom}), 127.7, 128.2 (CH_{arom}), 129.4, 129.5 (CH_{arom}), 131.0, 146.8, 149.3 (C=O), 162.4 (C=O).

Acid-catalyzed transformation of 3*H*-pyrazole (2). 3*H*-Pyrazole **1**, 0.2 g (0.6 mmol), was dissolved in 20 mL of glacial acetic acid, and two drops of concentrated sulfuric acid were added at 20°C. The mixture spontaneously warmed up, and a solid precipitated. The mixture was diluted with 20 mL of cold water, and the precipitate was filtered off, washed with water until neutral washings, and dried under reduced pressure. Yield 0.14 g (87%) of **14**, mp 294–295°C.

X-Ray analysis of 1*H*-pyrazoles 7 and 13. The crystallographic data, parameters of X-ray diffraction experiments, and structure refinement parameters are collected in Table 1, and the molecular structures of **7** and **13** are shown in Figs. 1 and 2. The X-ray diffraction data were collected using an XtaLAB Pro MM003 Kappa Single diffractometer (Mo K_α radiation, λ 0.71073 Å; ω-scanning). The primary structures were solved by direct methods using SHELX [50]. The positions of other atoms, including hydrogens, were determined by the difference syntheses of electron density and were refined against $|F|^2$ by the least squares method. The positions of hydrogen atoms were refined in the general least squares cycle in isotropic approximation, and the positions of methyl hydrogen atoms were refined according to the riding model. The X-ray diffraction data for compounds **7** and **13** were deposited to the Cambridge Crystallographic Data Centre (CCDC entry nos. 1548070 and 1530546, respectively). The molecular structures were visualized using ORTEP-3 [53].

This study was performed in part in the framework of the base part of state assignment to high education and scientific institutions in the sphere of research activity (project no. 3.6502.2017/BCh).

REFERENCES

1. Van Alphen, J., *Recl. Trav. Chim. Pays–Bas*, 1943, vol. 62, p. 485.
2. Van Alphen, J., *Recl. Trav. Chim. Pays–Bas*, 1943, vol. 62, p. 491.
3. Hüttel, R., Franke, K., Martin, H., and Riedl, J., *Chem. Ber*., 1960, vol. 93, p. 1433.
4. Pérez-Aguilar, M.C. and Valdés, C., *Angew. Chem., Int. Ed*., 2013, vol. 52, p. 1.
5. Hao, L., Hong, J.-J., Zhu, J., and Zhan, Z.-P., *Chem. Eur. J*., 2013, vol. 19, p. 5715.
6. Gladow, D., Doniz-Kettenmann, S., and Reissig, H.-U., *Helv. Chim. Acta*, 2014, vol. 97, p. 808.
7. Pérez-Aguilar, M.C. and Valdés, C., *Angew. Chem., Int. Ed*., 2015, vol. 54, p. 13729.
8. Nagai, T. and Hamaguchi, M., *Org. Prep. Proced. Int*., 1993, vol. 25, p. 403.
9. Sammes, M.P. and Katritzky, A.R., *Adv. Heterocycl. Chem*., 1983, vol. 34, p. 1.
10. Vasin, V.A., Masterova, Yu.Yu., Razin, V.V., and Somov, N.V., *Russ. J. Org. Chem*., 2014, vol. 50, p. 1323.
11. Vasin, V.A., Masterova, Yu.Yu., Bezrukova, E.V., Razin, V.V., and Somov, N.V., *Russ. J. Org. Chem*., 2015, vol. 51, p. 874.
12. Vasin, V.A., Razin, V.V., Bezrukova, E.V., and Petrov, P.S., *Russ. J. Org. Chem*., 2016, vol. 52, p. 862.
13. Sammes, M.P. and Katritzky, A.R., *Adv. Heterocycl. Chem*., 1983, vol. 34, p. 53.
14. Baumes, R., Elguero, J., Jacquier, R., and Tarrago, G., *Tetrahedron Lett*., 1973, vol. 14, p. 3781.
15. Bramley, R.K., Grigg, R., Guilford, G., and Milner, P., *Tetrahedron*, 1973, vol. 29, p. 4159.
16. Guillerm, G., L'Honoré, A., Veniard, L., Pourcelot, G., and Benaim, J., *Bull. Soc. Chim. Fr*., 1973, p. 2739.
17. Baumes, R., Elguero, J., Jacquier, R., and Tarrago, G., *J. Heterocycl. Chem*., 1973, vol. 10, p. 763.
18. Abbott, P.J., Acheson, R.M., Flowerday, R.F., and Brown, G.W., *J. Chem. Soc., Perkin Trans. 1*, 1974, p. 1178.
19. Dürr, H., Schmidt, W., and Sergio, R., *Justus Liebigs Ann. Chem*., 1974, p. 1132.
20. Dürr, H. and Schmidt, W., *Justus Liebigs Ann. Chem*., 1974, p. 1140.
21. Dürr, H. and Sergio, R., *Chem. Ber*., 1974, vol. 107, p. 2027.
22. Razin, V.V., *Zh. Org. Khim*., 1975, vol. 11, p. 1457.
23. Sharp, J.T., Findlay, R.H., and Thorogood, P.B., *J. Chem. Soc., Perkin Trans. 1*, 1975, p. 102.
24. Dingwall, J. and Sharp, J., *J. Chem. Soc., Chem. Commun*., 1975, p. 128.

25. Komendantov, M.I. and Bekmukhametov, R.R., *Chem. Heterocycl. Compd*., 1975, vol. 11, p. 68.
26. Franck-Neumann, M. and Dietrich-Buchecker, C., *Tetrahedron Lett*., 1976, vol. 17, p. 2069.
27. Heydt, H. and Regitz, M., *Justus Liebigs Ann. Chem*., 1977, p. 1766.
28. Domnin, I.N., Zhuravleva, E.F., Serebrov, V.L., and Bekmukhametov, R.R., *Chem. Heterocycl. Compd*., 1978, vol. 14, p. 879.
29. Leach, J.C.L. and Wilson, J.W., *J. Org. Chem*., 1978, vol. 43, p. 4880.
30. Stanley, K.L.M., Dingwall, J., Sharp, J.T., and Naisby, T.W., *J. Chem. Soc., Perkin Trans. 1*, 1979, p. 1433.
31. Leigh, W.J. and Arnold, D.R., *Can. J. Chem*., 1979, vol. 57, p. 1186.
32. Mataka, S. and Tashiro, M., *J. Org. Chem*., 1981, vol. 46, p. 1929.
33. Mataka, S., Ohshima, T., and Tashiro, M., *J. Org. Chem*., 1981, vol. 46, p. 3960.
34. Komendantov, M.I., Zavgorodnyaya, A.P., Domnin, I.N., and Bekmukhametov, R.R., *Zh. Org. Khim*., 1986, vol. 22, p. 1541.
35. Majchrzak, M.W., Jefferson, E.A., and Warkentin, J., *J. Am. Chem. Soc*., 1990, vol. 112, p. 2449.
36. Frampton, S., Majchrzak, M.W., and Warkentin, J., *Can. J. Chem*., 1991, vol. 69, p. 373.
37. Jefferson, E.A. and Warkentin, J., *J. Am. Chem. Soc*., 1992, vol. 114, p. 6318.
38. Jefferson, E.A. and Warkentin, J., *J. Org. Chem*., 1994, vol. 59, p. 455.
39. Belaissaoui, A., Jacquot, S., Morpain, C., Schmitt, G., and Laude, J.V.B., *Can. J. Chem*., 1997, vol. 75, p. 523.
40. Yen, Y., Chen, S.-F., Heng, Z.-C., Huang, J.-C., Kao, L.-C., Lai, C.-C., and Liu, R.S.H., *Heterocycles*, 2001, vol. 55, p. 1859.
41. Fedorov, A.A., Duisenbaev, Sh.E., Razin, V.V., Kuznetsov, M.A., and Linden, E., *Russ. J. Org. Chem*., 2007, vol. 43, p. 231.
42. Srhrader, L., *Chem. Ber*., 1971, vol. 104, p. 941.
43. Ege, G. and Huhn, B., *Justus Liebigs Ann. Chem*., 1972, vol. 763, p. 39.
44. Razin, V.V. and Rud', E.M., *Zh. Org. Khim*., 1976, vol. 12, p. 689.
45. Komendantov, M.I., Bekmukhametov, R.R., and Domnin, I.N., *Tetrahedron*, 1978, vol. 34, p. 2743.
46. Razin, V.V., Barantseva, A.R., and Gulechko, V.S., *Zh. Org. Khim*., 1988, vol. 24, p. 1875.
47. Reissig, H.-U. and Huisgen, R., *J. Am. Chem. Soc*., 1979, vol. 101, p. 3648.
48. Reimlinger, H., *Chem. Ber*., 1967, vol. 100, p. 3097.
49. Ege, G., *Tetrahedron Lett*., 1963, vol. 4, p. 1667.
50. Sheldrick, G.M., *Acta Crystallogr., Sect. A*, 2008, vol. 64, p. 112.
51. Farrugia, L.J., *J. Appl. Crystallogr*., 1999, vol. 32, p. 837.
52. CrysAlis PRO 1.171.39.6b, Rigaku Oxford Diffraction, 2015.
53. Burnett, M.N. and Johnson, C.K., *ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, Oak Ridge National Laboratory Report ORNL-6895, 1996.