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Thermal and Acid-Catalyzed Transformations of 3*H*-Pyrazoles Obtained from Diphenyldiazomethane and Methyl Phenylpropiolate

A. A. Fedorov[a], Sh. E. Duisenbaev[a], V. V. Razin[a], M. A. Kuznetsov[a], and E. Linden[b]

[a]*St. Petersburg State University, St. Petersburg, 19850 Russia*
e-mail: vvrazin@mail.ru
[b]*Institut fur Organische Chemie, Universitat Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland*

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Abstract—Reaction of diphenyldiazomethane with methyl phenylpropiolate in diethyl ether alongside the expected methyl triphenyl-3*H*-pyrazole-4- and -5-carboxylates (**I** and **II**) (38 and 24%) gave rise also to 8% of methyl 3,5-diphenyl-1-(1-ethoxyethyl)-1*H*-pyrazole-4-carboxylate. The main thermolysis product obtained from 4-methoxycarbonyl derivative **I** was methyl 1,3,5-triphenyl-1*H*-pyrazole-4-carboxylate, whereas from regioisomer **II** formed predominantly methyl 4,4,5-triphenyl-4*H*-pyrazole-3-carboxylate and 1-methoxycarbonyl-2,3,3-triphenylcyclopropene that was a minor product of 3*H*-pyrazole **I** thermolysis. Addition of concn. H_2SO_4 to the solutions of methyl triphenyl-3*H*-pyrazole-4- and -5-carboxylates in AcOH resulted in fast regioselective isomerization of the 3*H*-pyrazole derivatives into the corresponding 4*H*-pyrazoles.

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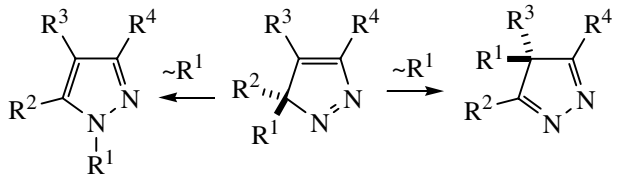
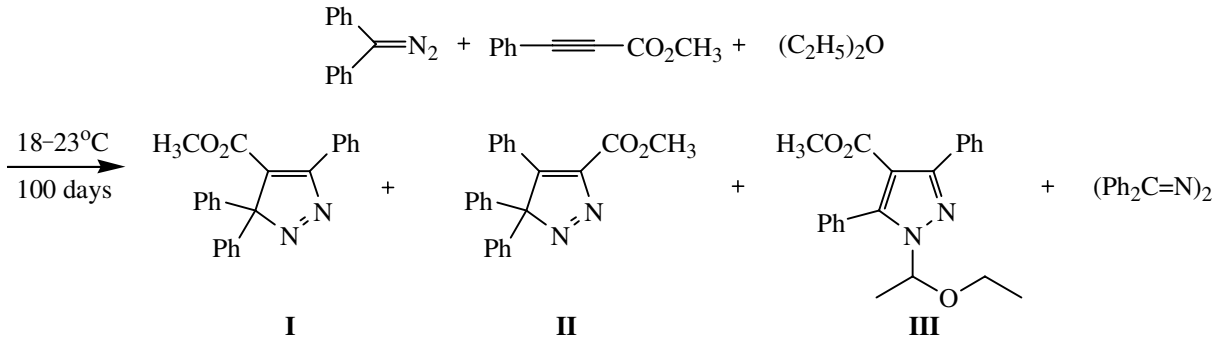
3*H*-Pyrazoles rearrangement with the migration of substituents around the ring has been discovered more than half-century ago and since that time is known as van Alphen–Huttel rearrangement [1, 2]. Much later it was interpreted in the framework of Woodward–Hoffmann rule as resulting from a suprafacial 1,5-sigmatropic shift [3]. Depending on the direction of the substituent migration from C^3 atom this sigmatropic rearrangement of a substituted 3*H*-pyrazole **A** can yield either aromatic 1*H*-pyrazole **B** (shift to N^2 atom), or nonaromatic 4*H*-pyrazole **C** (shift to C^4 atom) [4]. Yet due to subsequent 1,5-shifts 4*H*-pyrazole **C** can finally also transform into aromatic 1*H*-pyrazole of **B** type, but with another position of the substituents [4–7].



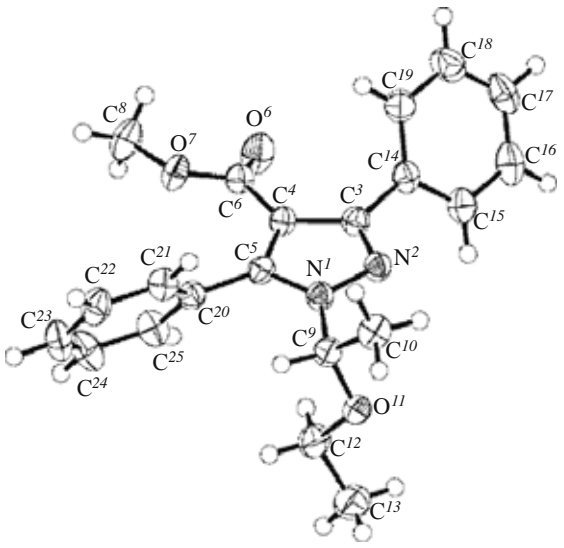
At the same time the effect of the nature and position of substituents in the 3*H*-pyrazoles on the migration direction is not yet clearly understood and therefore requires further investigations. We carried out in this study a van Alphen–Hüttel rearrangement of two isomeric 3*H*-pyrazoles **I** and **II** distinguished by positions of substituents at C^4 and C^5 atoms. Beside the purely thermal reaction we investigated transformations of compounds **I** and **II** at the treatment with a strong acid.

We applied to the preparation of initial 3*H*-pyrazoles **I** and **II** the known reaction of diphenyldiazomethane with methyl phenylpropiolate [8–13]. In the first report on this reaction [8] van Alphen succeeded in isolation of a single 3*H*-pyrazole that further was considered [9] to have structure **I** as a product of cycloaddition against the Auwers rule. The formation of a single adduct **I** was also described later in [10, 11], but then practically simultaneously [12, 13] the reaction was found to yield both possible isomers of 3*H*-pyrazole **I** and **II**, and in [13] their structural assignment was proved by photochemical denitration into isomeric indenes. We carried out a reaction of 1.5 equiv. of diphenyldiazomethane with methyl phenylpropiolate in ethyl ether (unlike [12, 13] where no solvent had been used) at room temperature (18–23°C) and in keeping with the data of [12, 13] we obtained both 3*H*-pyrazoles **I** and **II** that were separated by column chromatography on silica gel. However alongside the expected products, 3*H*-pyrazoles **I** (38%), **II** (24%), and benzophenone azine we isolated from the reaction mixture 8% of previously unknown 1*H*-pyrazole



III containing only two phenyl groups instead of three, and a fragment of the solvent.

The ratio of 3*H*-pyrazoles **I** and **II** obtained is well consistent with the data of [12] (62:38) and [13] (~2:1), and their structure is additionally confirmed by the features of ^{1}H and ^{13}C NMR spectra. For instance, the most downfield signal in the ^{1}H NMR spectrum of pyrazole **I** at 8.1 ppm, removed from the multiplets of the other aromatic protons by ~0.6 ppm, belongs to the *ortho* protons of the phenyl ring on the C^5 atom. Its downfield shift is caused by the contiguous N=N group, and also by the possibility of coplanarity of the phenyl substituent and the heterocycle, and then its *ortho*-protons should occur in the deshielding region of the π system of 3*H*-pyrazole. Unlike that, in regioisomer **II** the phenyl ring attached to C^4 atom should by steric reasons be located virtually normally to the plane of the five-membered ring. Therewith its *ortho*-protons are shielded by two neighboring phenyl groups and give a signal at 7.04 ppm.



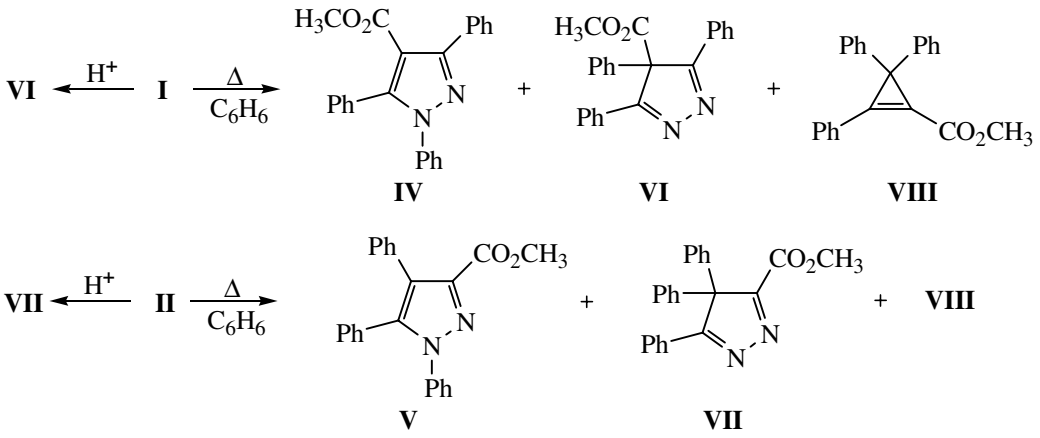
Structure of 1*H*-pyrazole **III** according to X-ray diffraction anlysis (ORTEP projection [16]; arbitrary numbering of atoms; ellipsoids of displacement are given in 50% probability).

In the ^{13}C NMR spectra of both 3,3-diphenyl-3*H*-pyrazoles **I** and **II** the chemical shift δ of C^3 atom ~110 ppm is characteristic (cf. [14]).

The prevalence of pyrazole **I**, the product of anti-Auwers addition, is likely due to steric factors: since the efficient volume of the phenyl group is considerably larger than that of the ester group, regioisomer **II** should suffer stronger destabilization caused by its repulsion from the *gem*-diphenyl moiety at C^3 atom (cf. the discussion on the regioselectivity of diazoalkanes cycloaddition to unsymmetrical alkynes in [15]).

Azines formation is a frequent event in diazoalkanes reactions [13], whereas the unusual for these processes product **III** is far more interesting. Its composition was confirmed by elemental anaysis, and the signals of all fragment of the molecule clearly appeared in the ^{1}H and ^{13}C NMR spectra. We failed to observe the molecular ion peak of pyrazole **III** in its mass spectrum, but the main fragment ions are in good agreement with the assumed structure. The position of the substituents in the five-membered ring was established from the nuclear Overhauser effect: the irradiation of the methoxy protons resulted in enhanced intensity of all the free aromatic signals, revealing that the ester group is adjacent to both phenyls. The structure of compound **III** was finally proved by X-ray diffraction analysis (see the figure).

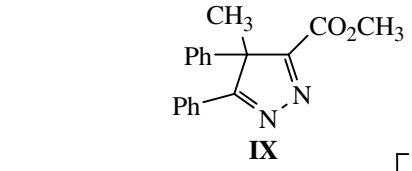
The way of 1*H*-pyrazole **III** formation is not clear, but presumably the process is of a radical character. Taking into account the similar position of substituents at the carbon atoms of compounds **I** and **III** it may be concluded that substance **III** originates from the secondary transformations of pyrazole **I**. However we failed to obtain it from pyrazole **I**. 1*H*-Pyrazole **III** was neither obtained by keeping the solution of compound **I** in ethyl ether at 18–23°C for ~3 months, nor by heating at 90°C in a sealed ampule for 3 h the ether solution of 3*H*-pyrazole **I** with a catalytic amount of benzoyl peroxide.



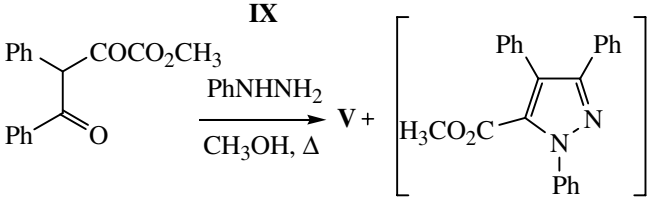
The thermolysis of 3*H*-pyrazoles **I** and **II** was carried out in benzene solution in a thick-walled sealed ampule. In both cases after 90 min at 135°C we observed complete disappearance of the initial compounds and formation of products of phenyl substituent migration to the adjacent nitrogens (1*H*-pyrazoles **IV** and **V**) and carbons (4*H*-pyrazoles **VI** and **VII**), and also of denitration product, cyclopropene **VIII**. The thermolysis of 3*H*-pyrazole **I** gave a mixture of 1*H*-pyrazole **IV**, 4*H*-pyrazole **VI**, and cyclopropene **VIII** in a ratio ~75:20:5, and of 3*H*-pyrazole **II**, a mixture of 1*H*-pyrazole **V**, 4*H*-pyrazole **VII**, and cyclopropene **VIII** in a ratio ~10:50:40.

Cyclopropene **VIII** was identified by comparison with an authentic sample that we had described previously [17]. The structure of thermolysis products of 3*H*-pyrazole **I**, compounds **IV** and **VI**, was established in [10, 11] and was additionally confirmed in our study by ^{13}C NMR spectra. Besides 1*H*-pyrazole **IV** was identified by its ^{1}H NMR spectrum with a published spectrum of a compound synthesized by another method [18]. Individual samples of 4*H*-pyrazoles **VI** and **VII** we isolated in the experiments on acid isomerization of 3*H*-pyrazoles **I** and **II** (see further); the structure of previously unknown compound **VII** was proved by the combination of its spectral data, in particular, by their comparison with those of its already known methyl analog **IX** [19]. Chromophore Ph–C=N–N=C–CO_2CH_3 common for these compounds results in the presence in their UV spectra of a strong long-wave absorption band: for pyrazole **VII** λ_{max} 303 nm (log ε 4.22), for compound **IX** λ_{max} 300 nm (log ε 4.11) [19]. It is also significant that the chemical shifts of C^3 and C^5 atoms of 4*H*-pyrazoles **VII** and **IX** in the ^{13}C NMR spectra virtually coincide (with clearly different chemical shifts of C^4atoms).

1*H*-Pyrazole **V** was identified with an authentic compound prepared from methyl 2,4 dioxo-3,4-diphenylbutanoate and phenylhydrazine.



IX



X

The identity of this obtained by us condensation product with 1*H* pyrazole **V** and not with its regioisomer **X** [20] follows even from the comparison of the melting points of our sample and compound **X** (the latter melts 74°C lower [20]). The final proof of the structure of 1*H*-pyrazole **V** and assignment of the signals in its NMR spectra we carried out using 2D NMR experiments (^{1}H–^{1}H- and ^{1}H–^{13}C-COSY, COLOC, 2D-NOESY). The decisive confirmation of structure **V** is the Overhauser effect between the *ortho*-protons of one of the phenyl rings (m, 7.01 ppm) and the protons of two other phenyl substituents: *ortho*-protons of the second phenyl ring (m, ~7.29 ppm), and protons of the third one appearing as a singlet at 7.33 ppm. This fact shows that all the three phenyl groups are close in space, impossible for structure **X**.

^{13}C NMR spectrum of 1*H*-pyrazole **V** registered without decoupling from protons provided a possibility to identify three downfield signals of quaternary carbon atoms at 142.2, 140.9, and 139.3 ppm. The first one is a triplet (*J* 3.3 Hz) and therefore belongs to C^5 atom attached to a phenyl ring (C^4 atom in 1*H*-pyrazoles

removed from nitrogens resonate far upfield). The signal at 140.9 ppm remains singlet and consequently can originate only from C^3 atom. The latter signal is split into a multiplet indicating that it belongs to C^i of the phenyl substituent, and the large chemical shift shows the contiguity of a nitrogen atom. In the COLOC-experiment appears a cross-peak between the most upfield signal of the two aromatic protons (m, 7.01 ppm) and a signal of C^5 atom of the five-membered ring (142.2 ppm). Therefore the signal at 7.01 ppm should be assigned to the *ortho*-protons of the phenyl ring at C^5 atom in agreement with the data on the Overhauser effect. One more important cross-peak is found between the narrow 5-protons singlet at 7.33 ppm and the signal of C^i substituent at a nitrogen atom (139.3 ppm). This is the only cross-peak for the latter signal, and we are thus enabled to assign this singlet at 7.33 ppm to all the five protons of the phenyl ring linked to N^1 atom. This assignment was confirmed by the $^1H-^{13}C$ COSY spectrum whose analysis in combination with the spectra $^1H-^1H$ COSY and 2D-NOESY permitted unambiguous assignment of practically all signals in the ^1H and ^{13}C NMR spectra of 1*H*-pyrazole **V**.

In the ^1H NMR spectra of obtained methoxycarbonyl-lpyrazoles a clear dependence of the chemical shift of the protons from the $COOCH_3$ was observed on its position in the hetero ring. In compounds **I, III, IV**, and **VI** where it is linked to C^4 and therewith from the both sides it is shielded by the phenyl substituents the corresponding singlet appears in the region δ 3.52–3.68 ppm. In pyrazoles **V, VII**, and **IX** the OCH_3 group occurs in the deshielding field of the C=N bond, and the respective signal suffers a downfield shift to δ 3.79–3.88 ppm. The maximum value of 3.94 ppm the chemical shift of these protons attains in the neighborhood of the N=N bond in 3*H*-pyrazole **II**.

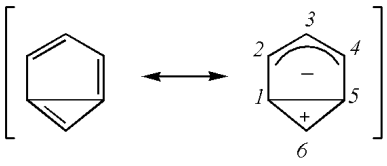
An unambiguous identification of 4*H*-pyrazoles **VI** and **VII** was based on their ^{13}C NMR spectra where the characteristic signal was that of C^4 atom at 76.2 (**VI**) and 77.9 (**VII**) ppm. Sharp reduction of the number of signals in the spectrum of compounds **VI** and double intensity of some among them confirm its symmetrical structure. Note also that the signals of C^3 and C^5 atoms in the spectrum of 4-phenyl-1*H*-pyrazole **V** appear at 141.0 and 142.2 ppm respectively, whereas in going to 4-methoxycarbonyl-1*H*-pyrazoles **III** and **IV** the signals suffer downfeld shift to ~147 and 153 ppm.

The data on thermolysis were published only for 3*H*-pyrazole **I** [10, 11]. It was reported that the heating of its melt at ~100°C gave a mixture of pyrazoles **IV** and **VI** in a ratio 3.6:1 [10], and at the thermolysis of its solution in *o*-xylene at 135°C [11] alongside the mixture of compounds **IV** and **VI**, 6:1, also 8% of cyclopropene **VIII** was obtained. Our data are in agreement with the results of [10, 11] and confirm the formation in thermolysis of 3*H*-pyrazole **I** of cyclopropene **VIII** that once has been considered unexpected [21].

The comparison of thermolysis results for isomeric 3*H*-pyrazoles **I** and **II** reveals considerable difference in their behavior. The main thermolysis product of 4-methoxycarbonyl derivative **I** is aromatic 1*H*-pyrazole **IV** whereas regioisomer **II** undergoes predominantly migration of a phenyl group to a carbon atom leading to the formation of 4*H*-pyrazole **VII**. The formation of cyclopropene **VIII** competes successfully with the latter process, but in the thermolysis of pyrazole **I** cyclopropene **VIII** is a minor product.

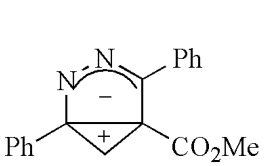
The presence of a mineral acid is known to accelerate significantly the van Alphen–Hüttel rearrangement [22]. We showed that adding concn. H_2SO_4 to a solution of 3*H*-pyrazoles **I** and **II** in acetic acid already at 20°C resulted in their regioselective isomerization (and exclusively in isomerization!) into 4*H*-pyrazoles **VI** and **VII** respectively. Formerly at heating 3*H*-pyrazole **I** in acetic acid solution at 80–90°C for 3 h was obtained a mixture of pyrazoles **IV** and **VI** in a ratio 1:1.25 [11], quite different in composition both from the products of the pure thermolysis and the acid-catalyzed process; the reaction under the above conditions presumably followed both routes.

Now we should focus on the discussion of results of thermal and acid-catalyzed transformations of 3*H*-pyrazoles **I** and **II**. We applied to the interpretaion of the regioselectivity of their thermal isomerization regarded as 1,5-sigmatropic rearrangement the approach of M. Dewar who considered the transition state of this pericyclic reaction as topologically equivalent to the aromatic system of bicyclo-[3.1.0]hexatriene [23]. Since the system is nonalternating, it is polarized with electrons transfer from the three-membered to the five-membered ring, and it may be regarded as a combination of an allyl anion and cyclopropenylium cation [24].

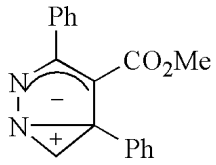


In keeping with above in the transition state atoms *1*, *5,* and *6* are charged positively, atoms *2* and *4* possess a negative charge, and the charge in position *3* is virtually zero. Then the introduction of electron-withdrawing substituents into positions *2* and *4* should enhance the stability of the bicyclo[3.1.0]hexatriene system, into positions *1* and *5,* cause its destabilization, and substituent in position *3* should not notably affect the process.

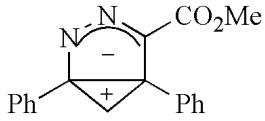
In the framework of this model the transition states for migration of 3-phenyl substituent in 3*H*-pyrazoles **I** and **II** to atoms C^4 and N^2 are as follows.



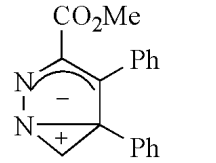
TS I(C)



TS I(N)



TS II(C)

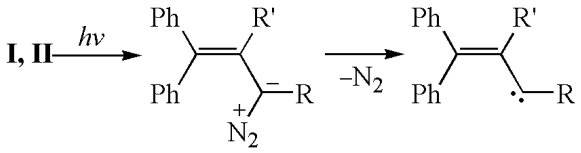


TS II(N)

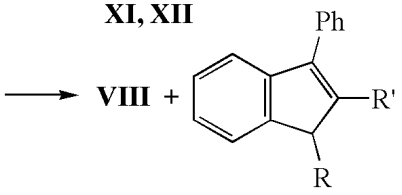
As seen, the transition state TS II(C) is more stable than TS I(C), and TS I(N) is more favorable, than TS II(N). Therefore we may expect that in the thermolysis products of 3*H*-pyrazole **II** the fraction of 4*H*-pyrazole would be greater, and that of 1*H*-pyrazole, smaller, than in the isomerization of 3*H*-pyrazole **I** as is found experimentally.

This approach provides also an understanding of the regioselectivity of the acid-catalyzed isomerization of 3*H*-pyrazoles **I** and **II**. Inasmuch as the protonation of compounds **I** and **II** occurs likely at the lone pair of the terminal nitrogen of the conjugation system (cf. [25]) it should lead in the corresponding pyrazolium cations to the stabilization of the structures TS I(C) and TS II(C) and in contrast to a strong destabilization of TS I(N) and TS II(N) due to the appearance of a positive charge in the cyclopropenyl fragment. Thus the prevalence of the 1,5-sigmatropic shift of the phenyl group to the carbon atom, i.e., of the formation of the corresponding 4*H*-pyrazole, sharply increases.

The thermal rearrangement of 3*H*-pyrazoles **I** and **II** suffers a competition with their denitration to cyclopropene **VIII**. The first scanty examples of 3*H*-pyrazoles denitration under thermolysis [11, 25] then turned essentially more numerous [26, 27], but the photolytic denitration of 3*H*-pyrazoles had been discovered earlier [28] and was better studied [4]. The photolysis of 3*H*-pyrazoles was shown to start with the ring opening into vinyldiazomethane derivatives that then eliminate a nitrogen molecule turning into vinylcarbenes. The latter further either isomerize into cyclopropenes (1,3-cyclization), or take part in other reactions [4]. In particular, the photolysis of 3*H*-pyrazoles **I** and **II** [13] proceeds through unsaturated diazo **XI** and **XII** leading in both cases to the formation of mixtures of the same cyclopropene **VIII** and indenes **XIII** and **XIV** corresponding to 1,5-cyclization of the respective vinylcarbenes.



XI, XII



XIII, XIV

I, XI, XIII, R = Ph, R' = CO_2Me; **II, XII, XIV**, R = CO_2Me, R' = Ph

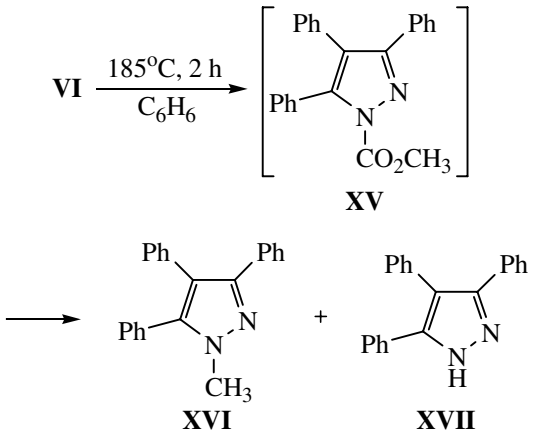
It is presumable that the thermal denitration of 3*H* pyrazoles occurs in the same fasion. It should be however taken into consideration that their isomerization into vinyldiazomethane derivatives is strongly endothermic (the enthalpy change for unsubstituted 3*H*-pyrazole is estimated at 26.8 kcal mol^{-1} [27]), and during the thermolysis with this process competes thermally permitted 1,5-sigmatropic shift. It is therefore understandable why the denitration of 3*H* pyrazoles under thermolysis occurs only in event they contain substituents capable to strongly stabilize the intermediate diazo compound (for instance, two phenyl groups attached to C^3 atom) [25–27].

The comparison of thermolysis results of 3*H*-pyrazoles **I** and **II** and with photolysis results of these compounds revealed two interesting facts. Firstly, the ratio of the denitration product to the products of rearrangement is quite different for compounds **I** and **II**. Secondly, unlike the photochemical denitration the thermal process yielded exclusively cyclopropene **VIII**. We failed to find indenes **XIII** or **XIV** in the corresponding reaction mixtures either by TLC or ^{1}H NMR spectroscopy.

The considerably higher yield of cyclopropene **VIII** in the thermolysis of 3*H*-pyrazole **II** than in reaction of its isomer **I** may be considered as indication of the higher rate of ring opening of compound **II** into the corresponding vinyldiazo compound **XII** caused by additional stabilization of the latter by the electronegative substituent (CO_2Me) at the carbon atom of the diazo group. Yet this assumption requires that the summary rates of the concurrent 1,5-sigmatropic rearrangements be nearly the same for pyrazoles **I** and **II**.

We believe that the second distinction is due to the possibility of a singlet-triplet transition in the course of the photochemical generation of vinylcarbene which is forbidden in thermolysis. Here we proceed from the assumption [13] on allowable 1,3-bonding into cyclopropene for a singlet vinylcarbene and favorable 1,5-cyclization for a triplet styrylcarbene.

The discoverers of van Alphen–Huttel rearrangement reported [1, 2] as the final product of 3*H*-pyrazole **I** transformations methyl-3,4,5-triphenyl-1*H*-pyrazole-1-carboxylate (**XV**). Since in our experiments we did not find it at all, it was presumable that the compound was a product of secondary transformations of the nonaromatic 4*H*-pyrazole **VI** under more stringent conditions. Although 4*H*-pyrazole **VI** was stated to be stable at 200°C [11], the heating of its benzene solution to 185°C for 2 h resulted in complete disappearance of the initial compound and in formation of 1 methyl-3,4,5-triphenyl-1*H*-pyrazole (**XVI**) and 3,4,5-triphenyl-1*H*-pyrazole (**XVII**) in a ratio ~2 : 1.



Possibly compounds **XVI** and **XVII** are the products of further transformations of the intermediately arising 1*H*-pyrazole **XV**. However since we failed to find the latter we cannot prove or disprove this assumption.

EXPERIMENTAL

Elemental analyses were performed on a C_2H_2N-analyzer Hewlett-Packard 185B. ^1H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra of solutions in $CDCl_3$ were registered on a spectrometer Bruker DPX-300 (if not indicated otherwise) using as internal references for ^1H NMR spectra the residual chloroform signal (δ 7.26 ppm), and for ^{13}C NMR spectra, the solvent resonance (δ 77.0 ppm). IR spectra were recorded on a spectrophotometer Perkin Elmer-1600 FT-IR, mass spectra were measured on Finnigan MAT-90 instrument in the electron impact mode (ionizing electrons energy 70 eV) and in the chemical ionization mode (reactant gas ammonia). UV spectrum of pyrazole **VII** in hexane was taken on a spectrophotometer Perkin Elmer M-402. Melting points were measured on Buchi Melting point B-540 instrument. The separation and purification of substances was carried out by column chromatography on silica gel L 5/40 (Chemapol). The composition of reaction mixture and fractions obtained by their separation, and also the purity of compounds isolated were determined by TLC on Silufol UV-254 plates (eluent heptane–ether, 1:1).

Diphenyldiazomethane [29], methyl phenylpropiolate [13], and methyl 2,4-dioxo-3,4-diphenylbutanoate [30] were obtained by published procedures.

X-ray diffraction analysis*. The single crystal of 1*H*-pyrazole **III** was obtained by slow evaporation of its solution in a mixture of ethyl ether and hexane, 1:1. The structural measurements were carried out on diffractometer Nonius KappaCCD [31]. The set of experimental reflections from the single crystal was obtained by ω-scanning on the MoK_α (λ 0.71073 Å) radiation with graphite monochromator at cooling with Oxford Cryosystems Cryostream 700. The data treatment was performed as suggested in [32]. The structure was solved by the direct method using software [33] and was refined by least-squares method in a full-matrix approximation by F^2. The atomic amplitudes for neutral nonhydrogen atoms were taken from [34], for hydrogens, from [35]. The effect of abnormal dispersion was taken into account in F_c [36], the values used for f' and f'' were from [37], the values of mass decrease factors, from [38]. The calculations were performed applying software package SHELXL97 [40].

* Free access to crystallographic data on compound **III** (CCDC-286780) is available from Cambridge Crystallographic Data Centre: www.ccdc.cam.ac.uk/data_request/cif.

X-ray diffraction data for pyrazole **III**. $C_{21}H_{22}N_2O_3$. *M* 350.42, colorless plates, crystal dimensions 0.07×0.17× 0.30 mm, orthorhombic crystal system, space group $Pca2_1$, *Z* 4, *a* 16.5694(9),

b 8.4759(4), *c* 13.5010(6) Å, *V* 1896.1(2) Å^3, D_X 1.194 g/cm^3, μ(MoK_α) 0.203 mm^{-1}, *T* 160 K, φ and ω scanning, transmission factors (min, max) 0.908, 0.974, $2\theta_{max}$ 55°, total measured 26432 reflexions, independent reflexions 1739, reflexions with $I > 2\sigma(I)$ 1563, 1739 reflexions were used in refining, 239 refined parameters, restrictions 1, *R* [for *F*, $I > 2\sigma(I)$ reflexions] 0.0381, $wR(F^2)$ (for all reflexions) 0.947 {$w = [\sigma^2(F_o^2) + (0.0527P)^2 ++ 0.2766P]^{-1}$, γdε $P = (F_o^2 + 2F_c^2)/3$}, quality factor 1.062, secondary extinction factor 0.014(2), Δ_{max}/σ 0.001, ΔC (max/min) = 0.16/–0.15 eA^{-3}.

Reaction of diphenyldiazomethane with methyl phenylpropiolate. A solution of 1.45 g (7.5 mmol) of diphenyldiazomethane and 0.80 g (5 mmol) of methyl phenylpropiolate in 25 ml of anhydrous ethyl ether was maintained in the dark at 10°C for 100 days in an air-tight thick-walled vessel. Within this period the color of the solution changed from dark-violet to pale pink. The solvent was evaporated in a vacuum, the residue was subjected to column chromatography on silica gel (eluent heptane–ether, 1:1). We isolated 0.28 g (20%) of benzophenone azine (R_f 0.79, mp 162–164°C [40]), 0.67 g (38%) of pyrazole **I** (R_f 0.56), 0.14 g (8%) of pyrazole **III** (R_f 0.34), and 0.42 g (24%) of pyrazole **II** (R_f 0.26).

Methyl 3,3,5-triphenyl-3*H*-pyrazole-4-carboxylate (I). mp 102.4–103.5°C [2]. IR spectrum, cm^{-1}: 3030 w, 2952 w, 1717 C, 1624 m, 1599 m, 1576 w, 1490 m, 1474 m, 1444 m, 1435 m, 1338 s, 1314 m, 1291 m, 1212 s, 1079 m, 1011 m, 970 m, 930 m, 754 m, 699 m. ^{1}H NMR spectrum, δ, ppm: 8.11–8.09 m (2H^O, 5-Ph), 7.54–7.52 m (3H$_{arom}$), 7.37–7.35 m (6H$_{arom}$), 7.30–7.28 m (4H$_{arom}$), 3.68 s (3H, MεO). ^{13}C NMR spectrum, δ, ppm: 164.3 (C=O), 157.0 (C^4), 138.7 (C^5), 135.0, 130.6, 129.8 br, 128.5 br (in total 18C$_{arom}$), 110.7 (C^3), 52.2 (MεO). Mass spectrum, chemical ionization, *m/z* (I_{rel}, %): 356 (24), 355 (100) $[M + H]^+$.

Methyl 3,3,4-triphenyl-3*H*-pyrazole-5-carboxylate (II). mp 103°C (99–100°C[13]). ^{1}H NMR spectrum, δ, ppm: 7.67–7.22 m (9H$_{arom}$), 7.17–7.15 doublet-like multiplet (4H, 3-Ph, H°, *J* 7.3 Hz), 7.06–7.03 doublet-like multiplet (2H, 4-Ph, H°, *J* 7.3 Hz), 3.94 s (3H, MεO). ^{13}C NMR spectrum, δ, ppm: 164.0, 162.1 (C=O and C^5), 143.2 (C^4), 133.2, 130.5, 130.1, 129.0, 128.8 br, 128.6 br, 128.0 (in total 18C$_{arom}$), 109.2 (C^3), 52.5 (MeO).

Methyl 3,5-diphenyl-1-(1-ethoxyethyl)-1*H*-pyrazole-4-carboxylate (III). mp 123–123.8°C. IR spectrum, cm^{-1}: 3008 w, 2973 w, 2940 w, 2903 w, 2879 w, 1715 s, 1485 m, 1459 m, 1436 m, 1377 m, 1316 m, 1234 m, 1197 m, 1146 m, 1119 s, 1043 m, 765 m, 697 m. ^{1}H NMR spectrum (spectrometer Bruker DPX-600, 600 MHz), δ, ppm: 7.73–7.71 m (2H$_{arom}$), 7.50–7.49 m (3H$_{arom}$), 7.43–7.27 m (5H$_{arom}$), 5.38 q (1H, CH–O, *J* 6.0 Hz), 3.52 s (3H, MeO), 3.31 d.q (1H, ^2J 14.1, ^3J 7.1 Hz) and 3.22 d.q (1H, ^2J 14.1, ^3J 7.1 Hz) OCH^{A}H^B; 1.7 d (3H, CHC$\underline{H}_3$, *J* 6.0 Hz), 1.08 t (3H, $CH_2C\underline{H}_3$, *J* 7.0 Hz). ^{13}C NMR spectrum, δ, ppm: 164.0 (C=O), 152.8 and 147.4 (C^3), 132.9, 130.0, 129.3, 129.2, 129.0, 128.9, 128.3, 128.2, 127.8 (12C$_{arom}$, C^4), 84.3 (OCH), 63.4 (OCH_2), 51.0 (MeO), 21.2 ($CH\underline{C}H_3$), 14.7 ($CH_2\underline{C}H_3$). Mass spectrum, electron impact *m/z* (I_{rel},%): 278 (22) [*M* – CH(Me)OEt], 247 (19) [*M* – CH(Me)OEt, – OMe]$^+$, 104 (10) [C(NH)Ph], 77 (18), 73 (35) [CH(Me)OEt], 45 (100) (OEt). Found, %: C 72.08; H 6.31; N 7.95. $C_{21}H_{22}N_2O_3$. Calculated, %: C 71.98; H 6.33; N 7.99.

Attempts to obtain 1*H*-pyrazole III from 3*H*-pyrazole I. A solution of 50 mg (140 μmol) of 3*H*-pyrazole **I** in 5 ml of anhydrous ethyl ether was kept at room temperature (18–23°C) in the dark for 90 days. The solvent was removed in a vacuum. The residue according to ^{1}H NMR spectrum and TLC data contained only initial pyrazole **I**.

A solution of 50 mg (140 μmol) of pyrazole **I** and 5 mg (20 μmol) of benzoyl peroxide in 3 ml was heated for 2 h in a thick-walled ampule at 90°C. The solvent was removed in a vacuum. The residue according to ^{1}H NMR spectrum contained initial pyrazole **I** with admixture of its thermolysis products (see below), but no compound **III**.

Thermolysis of 3*H*-pyrazoles I and II. A solution of 355 mg (1 mmol) of an appropriate 3*H*-pyrazole in 15 ml of benzene was maintained in a thick-walled ampule at 135°C for 50–90 min. TLC monitoring after 50 min indicated the presence in the reaction mixture of still considerable amounts of initial compounds, but within 90 min they completely disappeared. The solvent was removed in a vacuum, yields of reaction products were estimated from the intensity ratio of the corresponding methoxy protons in the ^{1}H NMR spectra. As a result of thermolysis of 3*H*-pyrazole **I** a mixture was obtained of pyrazoles **IV** and **VI** and cyclopropene **VIII** in a ratio ~ 75:20:5, and a mixture obtained from pyrazole **II** contained pyrazoles **V** and **VII** and cyclopropene **VIII** in a ratio ~ 10:50:40. By means of column chromato-

graphy we isolated in an individual state the main thermolysis product of compound **I** and two principal thermolysis products of compound **II**. The minor components of the reaction mixture were identified by comparison with authentic substances by TLC and the position of the methoxy protons in the ^{1}H NMR spectra.

Methyl 1,3,5-triphenyl-1*H*-pyrazole-4-carboxylate (IV). R_f 0.50, mp 139–140°C [2]. ^{1}H NMR spectrum, δ, ppm: 7.82–7.80 doublet-like multiplet ($2H_{arom}$), 7.49–7.47 m ($3H_{arom}$), 7.40–7.31 m ($10H_{arom}$), 3.63 s (3H, MεO). ^{13}C NMR spectrum, δ, ppm: 164.2 (C=O), 153.2, 146.3 (C^3, C^5), 139.1 (C^{and}, 1-Ph), 132.7, 130.3, 129.0, 128.7 br, 128.5, 128.3, 128.0, 127.9, 127.8, 125.4 ($17C_{arom}$, C^4), 51.2 (MeO).

Methyl 1,4,5-triphenyl-1*H*-pyrazole-3-carboxylate (V). A solution of 100 mg (0.35 mmol) of methyl 2,4-dioxo-3,4-diphenylbutanoate and 76 mg (0.7 mmol) of phenylhydrazine in 15 ml of methanol was heated at reflux for 92 h. The reaction mixture was kept for half a year, then the formed precipitate was separated and washed with methanol (2×10 ml). Yield 49.5 mg (40%), mp 180.6–182.4°C, R_f 0.33. IR spectrum, cm^{-1}: 3059 w, 2953 w, 1730 s, 1599 m, 1499 m, 1444 m, 1368 m, 1324 m, 1243 m, 1199 s, 1161 s, 1093 m, 1011 m, 784 m, 763 m, 701 s. ^{1}H NMR spectrum, δ, ppm: 7.33 s (5H, 1-Ph), 7.29–7.23 m (6H; 5H, 4-Ph; H^p, 5-Ph), 7.21–7.16 m ($2H^m$, 5-Ph), 7.02–6.99 m ($2H^o$, 5-Ph), 3.88 s (3H, MeO). ^{13}C NMR spectrum, δ, ppm: 162.7 q (C=O, J 4.2 Hz), 142.2 t (C^5, J 3.3 Hz), 141.0 C (C^3), 139.3 m (C^i, 1-Ph), 131.4 m (C^i, 5-Ph), 130.5 d.m (C^o 4-Ph), 130.3 d.m (C^o, 5-Ph), 128.8 d.m (C^m, 1-Ph), 128.4 d.m (C^p, 5-Ph), 128.2 d.m (C^m, 5-Ph), 128.1 d.m (C^p, 1-Ph), 127.6 d.m (C^m, 4-Ph), 127.1 d.m (C^p, 4-Ph), 125.6 d.m (C^o, 1-Ph), 124.9 m, 51.9 q (MeO, J 147.6 Hz). The multiplicity of signals and coupling values were obtained from the ^{13}C NMR spectrum registered without decoupling from protons. The values of direct coupling constants $^1J_{CH}$ in the phenyl substituents were ~160 Hz. The assignment of signals was based on the data of 2D NMR spectroscopy (^{1}H–^{1}H- and ^{1}H–^{13}C COSY, COLOC, 2D-NOESY). Mass spectrum, electron impact, m/z (I_{rel}, %): 355 (27), 354 (100) $[M]^+$, 323 (23), 321 (18), 296 (18), 295 (18), 180 (17), 77 (14). Found, %: C 77.90; H 5.10; N 7.84. $C_{23}H_{18}N_2O_2$. Calculated, %: C 77.95; H 5.12; N 7.90. M 354.41.

Methyl 3,4,5-triphenyl-4*H*-pyrazole-4-carboxylate (VI). mp 196–198°C (198–201°C [10]), R_f 0.26. ^{1}H NMR spectrum, δ, ppm: 7.88 d ($4H_{arom}$, J 6.5 Hz), 7.54–7.52 doublet-like multiplet ($2H_{arom}$, J 6.5 Hz), 7.39–7.29 m ($9H_{arom}$), 3.63 s (3H, MeO). ^{13}C NMR spectrum, δ, ppm: 174.4 ($C^{3,5}$), 166.9 (C=O), 131.5, 131.3, 129.4, 128.8 br, 128.6, 128.5, 127.1 ($8C_{arom}$), 76.2 (C^4), 53.4 (MeO).

Methyl 4,4,5-triphenyl-4*H*-pyrazole-3-carboxylate (VII). mp 179.3–180.3°C, R_f 0.20. UV spectrum, λ_{max}, nm (log ε): 303 (4.22). IR spectrum, cm^{-1}: 3059 w, 2946 w, 1729 C, 1598 w, 1551 w, 1514 m, 1493 m, 1441 m, 1339 s, 1194 m, 1144 s, 1034 w, 989 w, 952 w, 808 w, 773 m, 753 m, 699 s. ^{1}H NMR spectrum, δ, ppm: 7.80 d ($2H_{arom}$, J 7.3 Hz), 7.38–7.24 m ($13H_{arom}$), 3.79 s (3H, MεO). ^{13}C NMR spectrum, δ, ppm: 181.3 (C^5), 171.7 (C=O), 160.3 (C^3), 132.7, 131.9, 129.7, 129.0, 128.6, 128.5 br, 128.4, 128.3 ($18C_{arom}$), 77.9 (C^4), 52.7 (MeO). Mass spectrum, electron impact, m/z (I_{rel}, %): 327 (16), 326 (61), 312 (12), 311 (33), 294 (18), 268 (14), 267 (30), 266 (8), 265 (13), 252 (8), 251 (13), 219 (8), 207 (15), 193 (15), 192 (58), 191 (18), 190 (20), 166 (28), 165 (100), 164 (9), 105 (17), 103 (13). Found, %: C 77.73; H 5.16; N 7.83. $C_{23}H_{18}N_2O_2$. Calculated, %: C 77.95; H 5.12; N 7.90.

Methyl 2,3,3-triphenylcyclopropene-1-carboxylate (VIII). mp 127–128°C [19], R_f 0.71. ^{1}H NMR spectrum, δ, ppm: 7.93–7.91 m ($2H_{arom}$), 7.50–7.48 m ($3H_{arom}$), 7.37–7.33 m ($4H_{arom}$), 7.31–7.22 m ($6H_{arom}$), 3.95 s (3H, MeO). ^{13}C NMR spectrum, δ, ppm: 161.1 (C=O), 143.9 (C^1), 133.3 (C^2), 131.7, 131.5, 129.4, 128.3 br, 126.4, 125.9 ($18C_{arom}$), 109.9 (C^3), 52.4 (MeO).

Methyl 4-methyl-4,5-diphenyl-4*H*-pyrazole-3-carboxylate (IX). The sample was obtained in [19]. mp 104–105°C. ^{1}H NMR spectrum, δ, ppm: 7.75 d ($2H_{arom}$, J 7.2 Hz), 7.42–7.30 m ($6H_{arom}$), 7.22–7.17 m ($2H_{arom}$), 3.84 s (3H, OCH_3), 1.96 s (3H, CH_3). ^{13}C NMR spectrum, δ, ppm: 181.9 (C^3), 172.1 (C=O), 160.0 (C^5), 132.7, 131.9, 129.3, 128.9, 128.6, 128.3, 128.1, 125.7 (C_{arom}), 67.1 (C^4), 52.5 (OCH_3), 18.9 (CH_3).

Acid-catalyzed isomerization of 3*H*-pyrazoles I and II. To a solution of 100 mg (0.28 mmol) of 3*H*-pyrazole **I** or **II** in 10 ml of glacial acetic acid was added 0.1 ml (2 mmol) of concn. H_2SO_4, and the reaction mixture was left standing at room temperature (18–23°C). According to TLC 2 h later the initial pyrazoles disappeared, and in each case a single reaction product was obtained. The reaction was stopped by diluting the mixture with water, the products were extracted into ether (3×10 ml), the organic solution was washed with $NaHCO_3$ solution till the end of gas liberation, and then it was dried with $MgSO_4$. The residue after evaporating

the solvent was virtually pure product (TLC data). After recrystallization we obtained from compound **I** 60 mg (60%) of 4*H*-pyrazole VI, and from compound **II** 55 mg (55%) of 4*H*-pyrazole **VII**.

Thermolysis of 4*H*-pyrazole VI. A solution of 100 mg (0.28 mmol) of 4*H*-pyrazole **VI** in 6 ml of benzene was heated for 2 h at 185°C in a thick-walled ampule. The reaction mixture became colorless solution with a white precipitate. According to TLC the initial pyrazole disappeared, and two thermolysis products were present. After separation on a column charged with 15 g of silica gel (eluent a mixture hexane–ethyl ether, 2:1) we obtained 53 mg (61%) of pyrazole **XVI** and 22 mg (26%) of pyrazole **XVII**.

1-Methyl-3,4,5-triphenyl-1*H*-pyrazole (XVI). mp 189.8–190.2°C (191–192°C [41]). ^{1}H NMR spectrum, δ, ppm: 7.49–7.46 m ($2H_{arom}$), 7.38–7.36 m ($3H_{arom}$), 7.28–7.23 m ($5H_{arom}$), 7.18–7.16 m ($3H_{arom}$), 7.06–7.03 m ($2H_{arom}$), 3.88 s (3H, Me). ^{13}C NMR spectrum, δ, ppm: 133.4, 130.4, 130.2, 128.5, 128.1 br, 127.3, 126.3 ($18C_{arom}$, C^3, C^4, C^5), 37.4 (Me). Mass spectrum, electron impact, *m/z* (I_{rel}, %): 311 (24), 310 (100) $[M]^+$, 309 (54), 294 (7), 267 (7), 166 (8), 147 (9), 118 (8), 77 (15). Found, %: C 85.19; H 5.86; N 8.97. $C_{22}H_{18}N_2$. Calculated, %: C 85.13; H 5.85; N 9.02. *M* 310.40.

3,4,5-Triphenyl-1*H*-pyrazole (XVII). mp 267–269°C (265–266°C [10]). ^{1}H NMR spectrum, δ, ppm: 7.39–7.36 m ($5H_{arom}$), 7.31–7.28 m ($8H_{arom}$), 7.21–7.20 m ($2H_{arom}$). Mass spectrum, electron impact, *m/z* (I_{rel}, %): 297 (24), 296 (100) $[M]^+$, 295 (67), 165 (22), 147 (9), 77 (8).

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