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# Synthesis of 3*H*-Pyrazoles by Reaction of Methyl and *p*-Tolyl Phenylethynyl Sulfones with Diphenyldiazomethane and Their Thermal and Acid-Catalyzed Transformations

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**Abstract**—Methyl and *p*-tolyl phenylethynyl sulfones reacted with diphenyldiazomethane in diethyl ether at 20°C to give 1,3-dipolar cycloaddition products both according and contrary to the von Auwers rule, sulfonyl-substituted 3*H*-pyrazoles at a ratio of 1 : 1.5 and 1.3 : 1, respectively. On heating in toluene for 2 h, the Auwers adducts underwent van Alphen–Hüttel rearrangement with 1,5-sigmatropic shift of one phenyl substituent to afford sulfonyl-substituted 4*H*-pyrazoles. Under analogous conditions, the anti-Auwers adducts rearranged into sulfonyl-substituted *N*-phenyl-1*H*-pyrazoles containing a small amount of the denitrogenation product, sulfonyl-substituted cyclopropene. The Auwers adducts, as well as 4*H*-pyrazoles resulting from their thermal rearrangement, were converted in 5–7 days at 20°C into 3,4,4-triphenyl-1*H*-pyrazol-5(4*H*)-one by the action of a catalytic amount of sulfuric acid in acetic acid. Under analogous conditions, the regioisomeric anti-Auwers adducts gave rise to 3,4,5-triphenyl-1*H*-pyrazole with an impurity of 4-(R-sulfonyl)-1,3,5-triphenyl-1*H*-pyrazoles.

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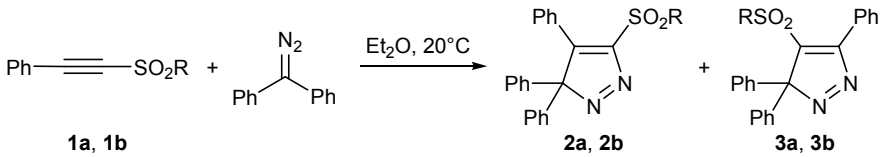
Functionally substituted 1*H*-, 3*H*-, and 4*H*-pyrazoles possess practically important properties, in particular high biological activity, which stimulates studies on their synthesis and applications [1–4]. One of the most efficient methods for the preparation of pyrazole derivatives is based on 1,3-dipolar cycloaddition of diazoalkanes to acetylenic compounds [5, 6]. Reactions of diazomethane and monosubstituted diazomethanes lead to the formation of 1*H*-pyrazoles. It is believed that initially formed unstable 3*H*-pyrazoles undergo aromatization to give 1*H*-pyrazoles via prototropic rearrangement. On the other hand, 3*H*-pyrazoles resulting from cycloaddition of disubstituted diazomethanes are quite stable. Among such 1,3-dipoles, diphenyldiazomethane has been studied most thoroughly. Reactions of diphenyldiazomethane with unsymmetrically substituted acetylenes, such as propynal and phenylpropynal, propynenitrile, methyl but-2-ynoate, and methyl 3-phenylprop-2-ynoate, were reported [7–13] to afford mainly two regioisomeric 3*H*-pyrazoles which were formed according and contrary to the von Auwers rule.* Thermal and acid-catalyzed transformations of these cycloadducts were studied, and it was found that van Alphen–Hüttel rearrangement occurred in each case [14, 15], which led to the formation of 1*H*- and/or 4*H*-pyrazole derivatives via 1,5-sigmatropic shift of the phenyl substituent. The regioselectivity of both cycloaddition and isomerization of the 3,3-diphenyl-3*H*-pyrazole derivative is largely determined by the effect of electron-withdrawing group in the initial dipolarophile [6].

In the present work we examined the addition of diphenyldiazomethane to acetylenic sulfones **1a** and **1b** and thermal and acid-catalyzed transformations of the resulting cycloadducts, sulfonyl-substituted 3*H*-pyrazoles. We have found only one relevant publication [16] in which the reaction of diphenyldiazomethane with propynyl phenyl sulfone was described. However,

* In the reaction of diphenyldiazomethane with propynal only Auwers 3*H*-pyrazole was obtained [7], whereas in the reaction with 3-phenylpropynenitrile, only the anti-Auwers adduct was formed [13].

**Scheme 1.**




**1a**, **1b** **2a**, **2b** **3a**, **3b**

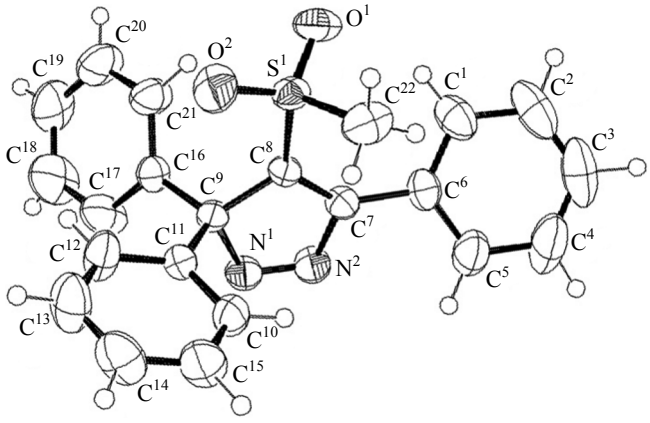
Hereinafter, R = Me (**a**), 4-$MeC_6H_4$ (**b**).

there were no data on van Alphen–Hüttel rearrangement of regioisomeric sulfonyl-substituted 3*H*-pyrazoles thus obtained. Dipolarophiles **1a** and **1b** reacted with 9-diazofluorene to give only Auwers 3*H*-pyrazoles [17] whose thermal, acid-catalyzed, and photoinduced transformations were studied.

The reactions of acetylenic sulfones **1a** and **1b** with diphenyldiazomethane were carried out in diethyl ether at 20°C for 5–7 days. From compound **1a** we obtained two possible regioisomers **2a** and **3a** at a ratio of 1 : 1.5 (according to the $^1$H NMR data) in favor of the anti-Auwers adduct. The ratio of regioisomeric pyrazoles **2b** and **3b** in the reaction with compound **1b** was 1.3 : 1, i.e., the Auwers adduct was the major product (Scheme 1). All compounds **2a**, **2b**, **3a**, and **3b** were isolated as pure substances, and their structure was confirmed by $^1$H and $^{13}$C NMR spectroscopy with account taken of specific spectral features of different regioisomers. Compound **3a** showed in the $^1$H NMR spectrum a two-proton signal at δ 8.3 ppm, which was located at a distance of ~0.7 ppm from the multiplet corresponding to the other aromatic protons. We assigned that signal to the *ortho* protons in the phenyl ring on $C^5$, and its strong downfield shift may be rationalized by deshielding effect of the neighboring N=N fragment (cf. [12]). By contrast, in the spectrum of **2a** all aromatic proton signals are gathered in the region δ 7.1–7.4 ppm. The proposed assignment is also supported by the large difference in the chemical shifts of the $SO_2Me$ protons (δΔ = 1.1 ppm). The $SO_2Me$ signal of **3a** is located in a stronger field (δ 2.39 ppm) due to shielding by the geminal phenyl substituents on $C^3$. Likewise, the $CPh_2$ moiety affects the position of signals of aromatic protons of the *p*-tolyl substituent (two doublets at δ 6.50 and 6.75 ppm) in the spectrum of **3b**; in the spectrum of **2b** all aromatic protons resonated in a weaker field (δ >7.0 ppm).

Compounds **2a**, **2b**, **3a**, and **3b** characteristically displayed in the $^{13}$C NMR spectra a signal at $\delta_C$ 110–113 ppm, which is typical of $C^3$ in 3*H*-pyrazoles. The IR spectra of **2a**, **2b**, **3a**, and **3b** contained strong absorption bands at ~1150 and 1320 $cm^{-1}$ due to symmetric and anti-symmetric stretching vibrations of the sulfonyl group [18]. The molecular ion peak in the mass spectra of these compounds had moderate intensity, and their fragmentation pattern involved elimination of the sulfonyl group and nitrogen molecule from the molecular ion. The structure of regioisomers **2** and **3** was finally proved by the X-ray diffraction data for compound **3a** (see figure).

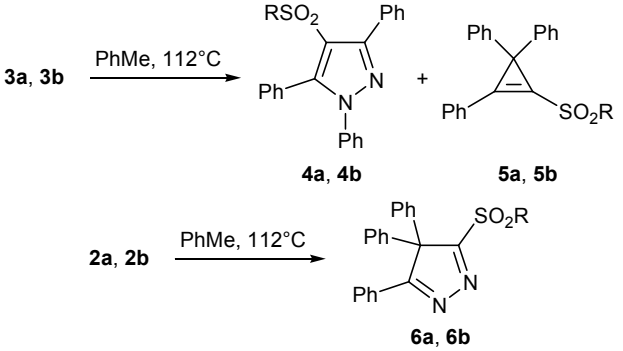
The relatively low regioselectivity of the cycloaddition of diphenyldiazomethane to acetylenic sulfones **1a** and **1b**, in contrast to complete regioselectivity of the cycloaddition of 9-diazofluorene [17] to the same dipolarophiles, is likely to be determined by different steric structures of these diazo compounds. In the reaction with planar 9-diazofluorene, steric factor is not significant, and the regioselectivity is controlled exclusively by the electronic factors. The benzene rings in the diphenyldiazomethane molecule are forced out of the $CN_2$ plane, which creates some steric hindrances to approach of the reactant to dipolarophile. Presumably, some difference in the regioselectivities of the cycloaddition of diphenyldiazomethane to dipolarophiles **1a** and **1b** is related to different effective volumes of the phenyl and sulfonyl substituents, on the one hand (conformational energies of the Ph and $SO_2Me$ groups are 2.80 and 2.50 kcal/mol, respectively [19]), and of the methylsulfonyl and phenylsulfonyl groups, on the other.




Structure of the molecule of 4-(methanesulfonyl)-3,3,5-triphenyl-3*H*-pyrazole (**3a**) according to the X-ray diffraction data.

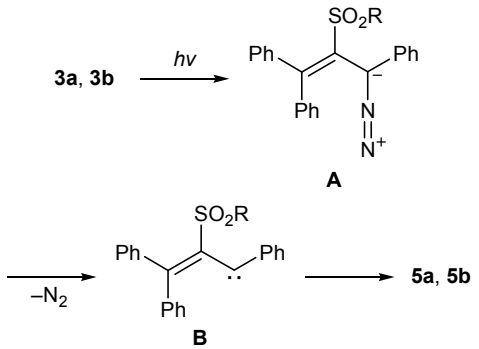
3*H*-Pyrazoles **2a**, **2b**, **3a**, and **3b** were subjected to thermolysis in boiling toluene (112°C, 2 h). Two products were obtained from each of compounds **3a** and **3b**, 1*H*-pyrazole **4a** (**4b**) and sulfonylcyclopropene **5a**, (**5b**) at a ratio of 5:1 or 9:1, respectively (according to the $^1$H NMR data). Under the same conditions, compounds **2a** and **2b** were converted into a single product, the corresponding 4*H*-pyrazole derivative **6a** or **6b** (Scheme 2).

**Scheme 2.**




Sulfonyl-substituted 1*H*-pyrazoles **4a** and **4b** were isolated in the pure state by silica gel column chromatography. Compound **4b** was identified by comparing its physical constants and spectral characteristics with those given in [20] where it was synthesized by a different method. The spectral parameters of **4a** were also satisfactorily consistent with the assumed structure. In particular, the $^{13}$C NMR spectrum of **4a** contained signals at $\delta_C$ ~146 and 152 ppm due to $C^3$ and $C^5$ of the 1*H*-pyrazole ring (cf. data for model compounds [12]). Cyclopropenyl sulfones **5a** and **5b** were identified in the reaction mixtures by $^1$H NMR; the corresponding pure compounds were isolated in the photolysis of 3*H*-pyrazoles **3a** and **3b**. Photolytic transformation of 3*H*-pyrazoles into cyclopropenes is a well known reaction [8, 10, 21] involving diazoalkane **A** and vinylcarbene **B** as intermediates (Scheme 3).

**Scheme 3.**

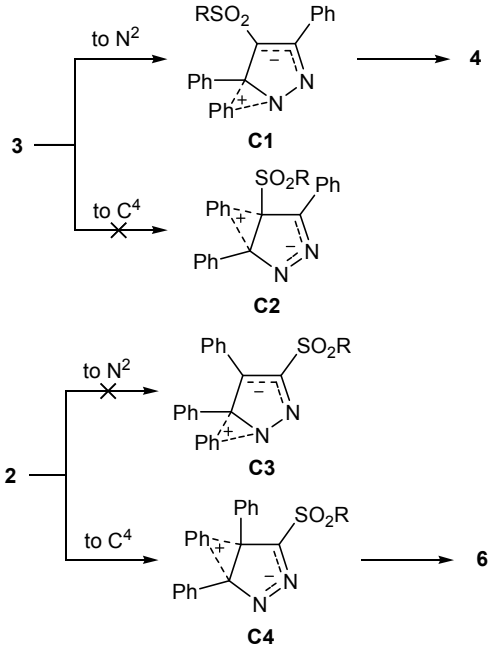



The structure of **5a** and **5b** was reliably confirmed by the $^1$H and and $^{13}$C NMR spectra. The IR spectra of **5a** and **5b** characteristically displayed a strong absorption band at ~1800 cm$^{-1}$ due to stretching vibrations of the disubstituted cyclopropene double bond [18, 22].

Compounds **6a** and **6b** were purified by crystallization, and their structure was determined on the basis of the IR, $^1$H and $^{13}$C NMR, and mass spectra. In the $^{13}$C NMR spectra of **6a** and **6b** we observed signals at $\delta_C$ ~80 ($C^4$) and ~180 ppm ($C^3$, $C^5$) which are typical of 4*H*-pyrazoles [23].

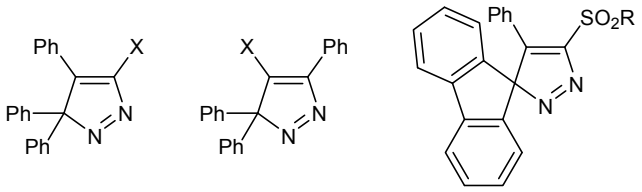
The results of thermal isomerization of 3*H*-pyrazoles **2a**, **2b**, **3a** and **3b** can be satisfactorily explained in terms of the Woodward–Hoffmann rules [24] assuming 1,5-sigmatropic shift of the phenyl group from $C^3$. However, the directions of this shift in regioisomers **2** and **3** are the opposite: strictly toward $N^2$ in **2** and strictly toward $C^4$ in **3**. While interpreting the regioselectivity of the thermal isomerization of pyrazoles **2** and **3** we followed the approach proposed in [12], according to which the transition states for the two possible transformations of **2** and **3** are simulated by polarized nonalternant diazabicyclo[3.1.0]hexatrienes **C1**–**C4** (Scheme 4; cf. [25, 26]).

**Scheme 4.**




Comparison of the results of thermal isomerization of 3*H*-pyrazoles **2** and **3** and their analogs **7** [12], **8** [9], **9** [12], and **11** [13] revealed a general relation. The presence of an electron-withdrawing substituent on $C^5$ favors the isomerization toward the formation of

4*H*-pyrazole, whereas *N*-phenyl-1*H*-pyrazole is formed as the major product when the same substituent is present in the 4-position.** In our case, as well as with cyano-substituted 3*H*-pyrazole **11**, this relation is clearly fulfilled, whereas lower regioselectivity is observed for 3*H*-pyrazoles **7**, **9**, and **10**. Presumably, the $SO_2R$ and CN substituents better stabilize negative charge in the isomerization transition state than do CHO and $CO_2Me$ groups {cf. Hammett constants $\sigma^-$: 1.13 ($SO_2Me$), 1.0 (CN), 0.74 ($CO_2Me$) [27]}.

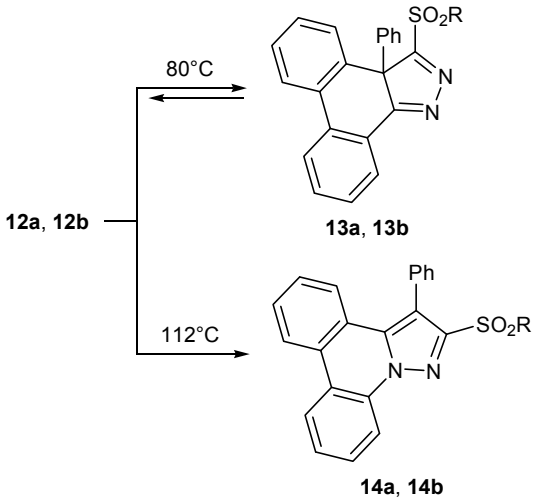


**7**, **8** **9–11** **12a**, **12b**

**7**, **9**, X = MeOCO; **8**, **10**, X = CHO; **11**, X = CN.

However, the thermolysis of known [17] 3*H*-pyrazoles **12a** and **12b** (analogs of **2**) at 80°C afforded 4*H*-pyrazoles **13** (analogs of **6**), in agreement with the behavior of 3*H*-pyrazoles **2**. On the other hand, unlike compounds **2**, heating of **12** or **13** at 112°C gave *N*-aryl-1*H*-pyrazole derivatives **14** (Scheme 5). This behavior of compounds **12** was rationalized [17] assuming that the isomerization of **12** into **13** is reversible at 112°C (but not at 80°C) and that the isomerization of **12** into more stable 1*H*-pyrazoles **14** is irreversible.

**Scheme 5.**



**12a**, **12b** **13a**, **13b** **14a**, **14b**

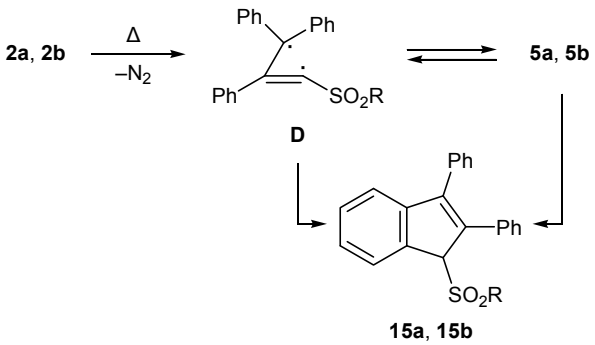
** An exception is 3*H*-pyrazole **10** [9] which readily undergoes thermal denitrogenation to the corresponding cyclopropene, so that van Alphen–Hüttel rearrangement products cannot be isolated.

Compounds **2** turned out to me appreciably more stable than their spiro analogs **12**.

With the hope of revealing reversibility of the isomerization of 3*H*-pyrazoles **2** into 4*H*-pyrazoles **6** we studied thermal transformations of these compounds at elevated temperature. When 3*H*-pyrazoles **2a** and **2b** were heated in boiling *o*-xylene (144°C) for 2 h, mixtures of 4*H*-pyrazoles **6a** and **6b** and ~10–15% of indenes **15a** and **15b** (denitrogenation products) were formed, whereas no cyclopropenes **5** were detected. Thermolysis of **2a** and **2b** in toluene at 180°C (40 min) under microwave irradiation afforded indenes **15a** and **15b** as the major products together with small amounts of three unidentified compounds. Pure indenes **15a** and **15b** were isolated by silica gel column chromatography, and their structure was confirmed by spectral methods. The $^1$H NMR spectra of **15a** and **15b** contained a singlet at δ 5.41 (5.62) ppm due to 1-H, and the $C^1$ signal appeared in the $^{13}$C spectrum at $\delta_C$ 73.5 and 74 ppm, respectively. A more rigorous proof was obtained by the NOE experiment for compound **15a**, which displayed long-range spin–spin coupling between the methyl protons and 1-H.

We believe that 3*H*-pyrazoles **2a** and **2b** at elevated temperature undergo partial or complete denitrogenation through intermediate diradical **D** whose recombination could give cyclopropene **5** or indene **15**. Furthermore, cyclopropenes **5**, like their analogs [28], are also potential precursors of **15** (Scheme 6). In fact, all these compounds at 150°C undergo completely regioselective cyclopropene–indene isomerization through diradical **D** [28]. The transformation at 180°C in 45–60 min yields only indenes **15** as the most stable products. Presumably, the rate of the isomerization of **5** into **15** at high temperature is higher than the rate of formation of **15** directly from 3*H*-pyrazoles **2**; therefore, cyclopropenes **5** were not detected in the reaction mixtures under these conditions. It should also be recognized that in this case the energy barrier to the

**Scheme 6.**

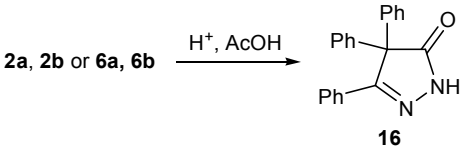


**2a**, **2b** **5a**, **5b** **D** **15a**, **15b**

denitrogenation of 3*H*-pyrazoles **2a** and **2b** is lower than the barrier to their transformation into the corresponding 1*H*-pyrazoles (analogs of **14**), so that the probability of the latter is low.

Addition of a catalytic amount of sulfuric acid to a solution of **2a** or **2b** in glacial acetic acid at 20°C led to the formation of 1*H*-pyrazol-5(4*H*)one **16**. The same compound was obtained from 4*H*-pyrazoles **6a** and **6b** under similar conditions (Scheme 7). In this respect, the behavior of 3*H*- and 4*H*-pyrazoles **2** and **6** was fully consistent with the behavior of their analogs **12** and **13** [17].

**Scheme 7.**

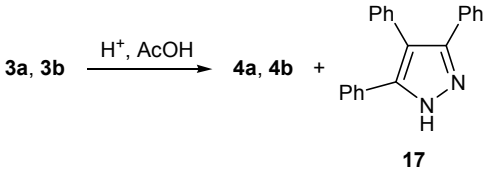



The structure of **16** was confirmed by the IR, $^1$H and $^{13}$C NMR, and mass spectra. The IR spectrum of **16** contained a strong carbonyl stretching vibration band at 1709 cm$^{-1}$ and weak absorption bands in the region 3060–3200 cm$^{-1}$ due to N–H vibrations [18]. In addition, the NH proton gave rise to a broadened singlet at δ 9.76 ppm in the $^1$H NMR spectrum. Characteristic signals in the $^{13}$C NMR spectrum of **16** were those located at $\delta_C$ 65.3 (C$^4$), 161.7 (C$^3$), and 179.5 ppm (C$^5$=O).

3*H*-Pyrazoles **3a** and **3b** in glacial acetic acid in the presence of a catalytic amount of $H_2SO_4$ were converted into the corresponding 1*H*-pyrazoles **4a** and **4b** and 3,4,5-triphenyl-1*H*-pyrazole **17**, the latter being the major product [ratio **4**:**17** 1:(3.5–4); Scheme 8]. Pure pyrazole **17** was isolated by crystallization from ethanol and was identified by comparing with published data [12, 29]. Pyrazoles **4a** and **4b** were identified in the reaction mixtures by $^1$H NMR.

The formation of pyrazolone **16** from compounds **2a** and **2b** under acidic conditions may be rationalized

**Scheme 8.**

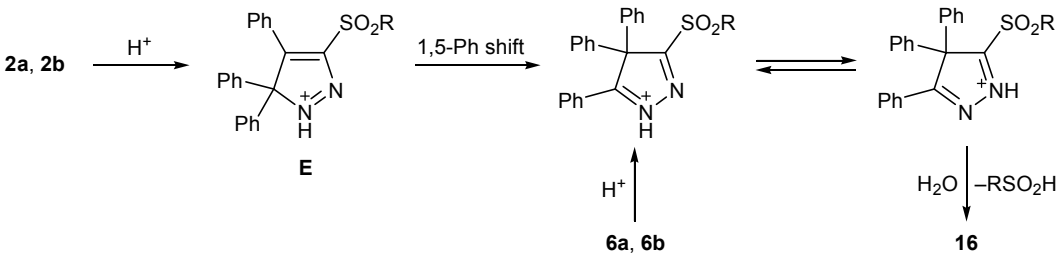



as shown in Scheme 9, where the key step is selective protonation of **2a** at the N$^2$ atom with formation of cation **E** which isomerizes into protonated 4*H*-pyrazole **6a**. Treatment of the reaction mixture with water afforded final product **16** as a result of proton transfer, hydration, and elimination of the corresponding sulfinic acid.

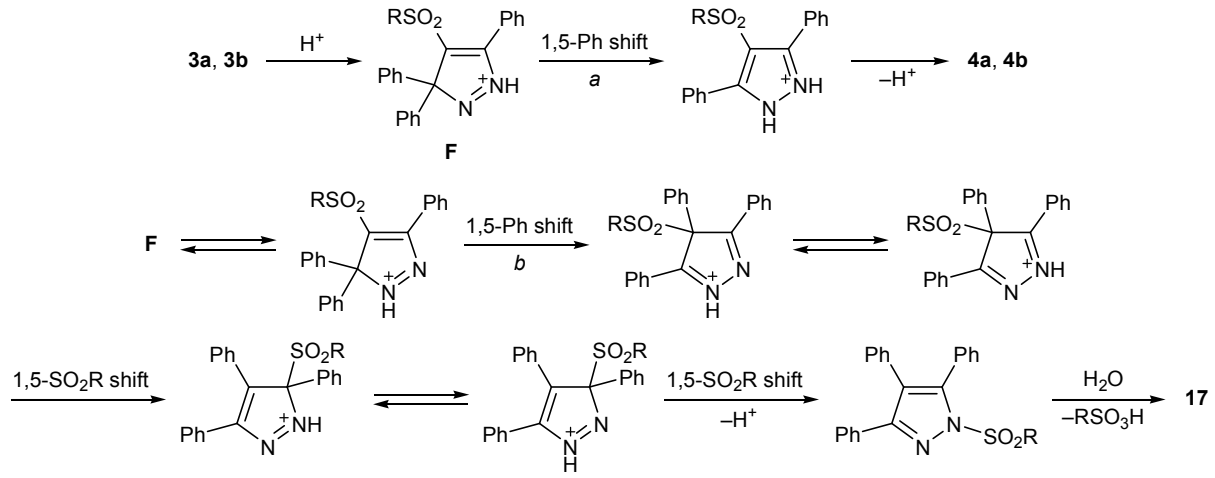
The acid-catalyzed transformation of 3*H*-pyrazoles **3a** and **3b** follows two competing pathways since their protonation is not as selective as the protonation of **2a** and **2b**. As a result, 1*H*-pyrazoles **4** (path *a*) and **17** (path *b*) are formed (Scheme 10). Path *b* involves intermediate protonated 4*H*- and 3*H*-pyrazoles and *N*-sulfonyl-1*H*-pyrazoles. Hydrolysis of the latter yields compound **17**. Examples of reversible concurrent protonation of structurally related 3*H*-pyrazoles at both nitrogen atoms, followed by rearrangement of the protonated forms with formation of different products, were reported in the literature [30] and were also observed by us previously [17].

In summary, by 1,3-dipolar cycloaddition of diphenyldiazomethane to sulfonyl-substituted acetylenes we have synthesized previously unknown regioisomeric sulfonyl-substituted 3,3-diphenyl-3*H*-pyrazoles and found that the direction of their thermal isomerization at 112°C with phenyl group migration to N$^2$ or C$^4$ is determined by the position of the electron-withdrawing group with respect to the geminal diphenyl moiety. On heating to 144°C and higher, 3*H*-pyrazoles lose nitrogen molecule to give 1-sulfonyl-2,3,3-triphenylcyclopropenes whose cyclopropene–indene isomerization affords 1-sulfonyl-2,3-diphenyl-1*H*-indenes. Due to reduction of the energy barrier, the acid-catalyzed van Alphen–Hüttel rearrangement of the Auwers

**Scheme 9.**



**Scheme 10.**



3*H*-pyrazoles occurs at room temperature and yields 3,4,4-triphenyl-1*H*-pyrazol-5(4*H*)-one through intermediate 4*H*-pyrazoles. Under analogous conditions, regioisomeric anti-Auwers 3*H*-pyrazoles are converted into mixtures of 4-sulfonyl-1,3,5-triphenyl- and 3,4,5-triphenyl-1*H*-pyrazoles. We plan to continue studies on rearrangements of sulfonyl-substituted 3*H*-pyrazoles with the goal of revealing general relations existing there.

## EXPERIMENTAL

The $^1$H and $^{13}$C NMR spectra were recorded on a Jeol JNM-ECX400 spectrometer at 400.1 and 100.6 MHz, respectively, using the residual proton and carbon signals of the deuterated solvents (δ 7.26 and 2.50 ppm, $\delta_C$ 77.0 and 39.5 ppm for $CDCl_3$ and DMSO-$d_6$, respectively) as reference. The IR spectra were recorded in KBr on an InfraLYuM FT-02 spectrometer with Fourier transform. The elemental analyses were obtained on a VarioMICRO CHNS analyzer. The mass spectra (electron impact) were recorded on a Konik RBK-HRGC5000B-MSQ12 (Konixbert HI-TECH, S.A.) Analytical TLC was performed on Sorbfil plates which were eluted with light petroleum ether–acetone (4:1) and developed in a iodine chamber. Silica gel Merck 60 (0.040–0.063 mm) was used for column chromatography (eluent light petroleum ether–acetone, 7:1 to 3:1). Microwave-assisted thermal isomerization was carried out in an Anton Paar Monowave 300 microwave oven (magnetron frequency 2455 MHz).

Ethynyl sulfones **1a** and **1b** [31] and diphenyldiazomethane [32] were prepared according to known methods.

**Reactions of compounds 1a and 1b with diphenyldiazomethane (*general procedure*).** A solution of 3.20 g (16.5 mmol) of diphenyldiazomethane in 30 mL of anhydrous diethyl ether was added to a solution of 15 mmol of compound **1a** or **1b** in 30 mL of the same solvent. The mixture was kept for 5–7 days at 20°C with protection from light. According to the $^1$H NMR data, the ratio of 3*H*-pyrazoles **2a** and **3a** (from **1a**) was 1:1.5, and of **2b** and **3b** (from **1b**), 1.3:1. Crystalline compounds **2** and **3** separated from the reaction solution. Compound **2** slowly crystallized first, and then pyrazole **3** separated. The products were successively isolated by filtration. Decomposition products of diphenyldiazomethane remained in solution. Attempts to separate mixtures of **2** and **3** by preparative TLC or column chromatography on silica gel or alumina were unsuccessful because the sorbent catalyzed chemical transformations leading to multicomponent mixtures of unidentified compounds. 3*H*-Pyrazoles **2a** and **2b** were completely converted into 1*H*-pyrazolone **16** on prolonged storage (for 1 month and more).

**5-(Methanesulfonyl)-3,3,4-triphenyl-3*H*-pyrazole (2a).** Yield 1.62 g (29%), yellow crystals, mp 154–155°C (from $CH_2Cl_2$–petroleum ether). IR spectrum, ν, cm$^{-1}$: 1609 w, 1590 w, 1493 m, 1447 m, 1323 s, 1146 v.s, 752 m, 694 m, 556 m. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 3.49 s (3H, $CH_3$), 7.14–7.16 m (4H, $H_{arom}$), 7.19–7.21 m (2H, $H_{arom}$), 7.28–7.42 m (9H, $H_{arom}$). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 43.2 ($CH_3$), 110.5 ($C^3$), 128.4 (2C), 128.6, 128.8 (4C), 129.2 (4C), 129.4 (2C), 130.0 (2C), 131.3, 132.5 (2C), 150.6 ($C^4$), 162.0 ($C^5$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 374 (40) $[M]^+$, 295 (13), $[M - SO_2CH_3]$, 267 (9) $[M - SO_2CH_3 - N_2]$, 192 (15), 190 (13), 165 (35), 77

(100), 51 (35). Found, %: C 70.60; H 4.82; N 7.41; S 8.67. $C_{22}H_{18}N_2O_2S$. Calculated, %: C 70.57; H 4.85; N 7.48; S 8.56. *M* 374.46.

**4-(Methanesulfonyl)-3,3,5-triphenyl-3*H*-pyrazole (3a).** Yield 2.84 g (51%), yellow crystals, mp 161–162°C (from $CH_2Cl_2$–petroleum ether). IR spectrum, ν, $cm^{-1}$: 1582 w, 1566 w, 1489 m, 1455 m, 1312 v.s, 1146 v.s, 953 m, 775 s, 702 v.s, 544 s. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.39 s (3H, $CH_3$), 7.36–7.42 m (10H, $H_{arom}$), 7.59–7.62 m (3H, $H_{arom}$), 8.31–8.33 m (2H, $H_{arom}$). $^{13}C$ NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 43.8 ($CH_3$), 113.4 ($C^3$), 128.6, 128.9 (4C), 129.0 (2C), 129.2 (4C), 129.3 (2C), 131.0 (2C), 131.9, 133.1 (2C), 148.0 ($C^4$), 157.3 ($C^5$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 374 (15) $[M]^+$, 295 (8) [$M$ – $SO_2CH_3$], 267 (41) [$M$ – $SO_2CH_3$ – $N_2$], 263 (100), 252 (96), 239 (79), 189 (99), 165 (94), 132 (97), 119 (85), 77 (72), 51 (69). Found, %: C 70.48; H 4.81; N 7.32; S 8.52. $C_{22}H_{18}N_2O_2S$. Calculated, %: C 70.57; H 4.85; N 7.48; S 8.56. *M* 374.46.

**5-(4-Methylbenzenesulfonyl)-3,3,4-triphenyl-3*H*-pyrazole (2b).** Yield 2.98 g (44%), yellow crystals, mp 151–152°C (from $CH_2Cl_2$–petroleum ether). IR spectrum, ν, $cm^{-1}$: 1597 w, 1559 w, 1489 m, 1443 m, 1316 m, 1154 v.s, 718 s, 752 m, 698 m, 583 v.s. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.45 s (3H, $CH_3$), 7.00–7.04 m (6H, $H_{arom}$), 7.25–7.37 m (10H, $H_{arom}$), 7.38–7.43 m (1H, $H_{arom}$), 7.93 d (2H, $H_{arom}$, $J$ = 8.4 Hz). $^{13}C$ NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 21.9 ($CH_3$), 110.1 ($C^3$), 128.1 (2C), 128.6 (4C), 128.9 (2C), 129.0 (4C), 129.1, 129.2 (2C), 129.6 (2C), 130.1 (2C), 130.7, 132.6 (2C), 136.7, 145.6, 151.4 ($C^4$), 161.7 ($C^5$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 450 (40) $[M]^+$, 386 (100), 295 (8) [$M$ – Ts], 267 (55) [$M$ – Ts – $N_2$], 266 (98), 252 (97), 190 (98), 166 (97), 91 (73), 77 (87), 65 (86), 51 (62). Found, %: C 74.69; H 4.89; N 6.03; S 7.15. $C_{28}H_{22}N_2O_2S$. Calculated, %: C 74.64; H 4.92; N 6.22; S 7.12. *M* 450.55.

**4-(4-Methylbenzenesulfonyl)-3,3,5-triphenyl-3*H*-pyrazole (3b).** Yield 2.12 g (31%), yellow crystals, mp 153–154°C (from $CH_2Cl_2$–petroleum ether). IR spectrum, ν, $cm^{-1}$: 1620 w, 1593 w, 1489 w, 1451 w, 1327 s, 1157 s, 752 m, 694 v.s, 586 s. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.22 s (3H, $CH_3$), 6.47 d (2H, $H_{arom}$, $J$ = 8.3 Hz), 6.75 d (2H, $H_{arom}$, $J$ = 8.1 Hz), 7.38–7.43 m (10H, $H_{arom}$), 7.50–7.59 m (3H, $H_{arom}$), 7.98–8.01 m (2H, $H_{arom}$). $^{13}C$ NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 21.6 ($CH_3$), 112.9 ($C^3$), 127.2 (2C), 128.4 (2C), 128.6 (4C), 128.9, 128.9 (2C), 129.1 (2C), 129.7 (4C), 130.8 (2C), 131.3, 133.5 (2C), 137.4, 144.8, 151.1 ($C^4$), 158.0 ($C^5$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 450 (52) $[M]^+$, 385 (49), 295 (9) [$M$ – Ts], 267 (49) [$M$ – Ts – $N_2$], 266 (95), 252 (97), 189 (97), 166 (100), 91 (89), 77 (82), 65 (94), 51 (69). Found, %: C 75.18; H 4.91; N 6.32; S 7.06. $C_{28}H_{22}N_2O_2S$. Calculated, %: C 74.64; H 4.92; N 6.22; S 7.12. *M* 450.55.

**X-Ray analysis of pyrazole 3a.** A yellow transparent prismatic single crystal of **3a** (0.31 × 0.26 × 0.16 mm) was grown from a solution in chloroform–llight petroleum ether (1 : 2). Total of 37041 reflection intensities were measured at 293(2) K on an Oxford Diffraction Xcalibur Gemini S automatic four-circle diffractometer (Mo$K_\alpha$ radiation, λ 0.71073 Å, graphite monochromator, Sapphire III CCD detector; ω-scanning, θ 3.45–30.5°, $-13 \le h \le 14$, $-29 \le k \le 29$, $-13 \le l \le 13$). Averaging of equivalent reflections left 5841 independent reflections ($R_{int}$ 0.0242), including 5010 reflections with $I > 2\sigma(I)$. The unit cell parameters were determined, and the reflection intensities were measured, using CrysAlisPro software [33]. A correction for absorption was applied empirically by the SCALE3 ABSPACK algorithm [33]. Monoclinic crystals, space group $P2_1/c$; unit cell parameters: $a$ = 9.8194(4), $b$ = 20.4689(7), $c$ = 9.6034(3) Å; β = 96.044(3)°; $V$ = 1919.48(12) $A^3$; *M* 374.44; $Z$ = 4; $d_{calc}$ = 1.296 g/$cm^3$; μ = 0.188 $mm^{-1}$; $F(000)$ = 784. The structure was solved by the direct method and was refined against $F^2$ by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms using SHELX97 [34] and WinGX [35]. Number of variables 316, goodness of fit 1.12; residual electron density $\rho_{min}/\rho_{max}$ –0.177/0.412 $\bar{e}$ $Å^{-3}$. Final divergence factors $R_1$ = 0.0618 [for reflections with $I > 2\sigma(I)$], $wR_2$ = 0.1757 (for all independent reflections). Hydrogen atoms were placed into geometrically calculated positions and were refined according to the riding model [$U$(H) = 1.5$U_{eq}$(C) for methyl groups, $U$(H) = 1.2$U_{eq}$(C) for other hydrogens]; weight scheme $w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 0.3640P]$, where $P = (F_o^2 + 2F_c^2)/3$. The molecular structure of **3a** was plotted using ORTEP-3 program [36]. The crystallographic data for compound **3a** were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 1055415).

**Thermolysis of 3*H*-pyrazoles 2 and 3 (*general procedure*).** A solution of 1 mmol of compound **2a**, **2b**, **3a**, or **3b** in 35 mL of toluene was heated for 2 h under reflux. The solvent was removed under reduced pressure, and the crude product was analyzed by $^1H$ NMR. 4*H*-Pyrazoles **6a** and **6b** (from **2**) were isolated by crystallization. The ratios of **4a** and **5a** (from **3a**) and

of **4b** and **5b** (from **3b**) were 5:1 and 9:1, respectively (calculated from the intensities of the methyl proton signals in the $^1$H NMR spectra). Pure compounds **4a** and **4b** were isolated by silica gel column chromatography. Cyclopropenes **5a** and **5b** were identified in the reaction mixtures by NMR.

**4-(Methanesulfonyl)-1,3,5-triphenyl-1*H*-pyrazole (4a).** Yield 0.27 g (72%), colorless crystals, mp 176–177°C (from $CH_2Cl_2$–petroleum ether). IR spectrum, ν, cm$^{-1}$: 1593 w, 1497 s, 1400 m, 1304 v.s, 1130 s, 791 m, 764 m, 694 m. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.77 s (3H, $CH_3$), 7.24–7.31 m (4H, $H_{arom}$), 7.38–7.43 m (4H, $H_{arom}$), 7.47–7.51 m (3H, $H_{arom}$), 7.88–7.90 m (2H, $H_{arom}$). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 44.9 ($CH_3$), 120.1 ($C^4$), 125.6 (2C), 127.9, 128.4 (2C), 128.4 (3C), 128.5, 129.1 (2C), 129.4, 130.0 (2C), 131.0 (2C), 131.3, 138.7, 145.7 and 151.6 ($C^3$, $C^5$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 374 (83) $[M]^+$, 373 (100), 295 (34) [$M$ – $SO_2CH_3$], 294 (51), 189 (47), 180 (22), 165 (9), 89 (9), 77 (75), 51 (35). Found, %: C 70.41; H 4.78; N 7.29; S 8.66. $C_{22}H_{18}N_2O_2S$. Calculated, %: C 70.57; H 4.85; N 7.48; S 8.56. *M* 374.46.

**4-(4-Methylbenzenesulfonyl)-1,3,5-triphenyl-1*H*-pyrazole (4b).** Yield 0.29 g (64%), colorless crystals, mp 212–213°C (from acetone–petroleum ether); published data [20]: mp 214–215°C (from $CHCl_3$–hexane). IR spectrum, ν, cm$^{-1}$: 1593 w, 1497 s, 1446 m, 1396 m, 1315 s, 1146 v.s, 764 m, 698 m, 598 m. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, $CH_3$), 6.70 d (2H, $H_{arom}$, $J$ = 8.0 Hz), 7.20–7.29 m (9H, $H_{arom}$), 7.32–7.36 m (2H, $H_{arom}$), 7.40–7.45 m (4H, $H_{arom}$), 7.69–7.72 m (2H, $H_{arom}$). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 21.6 ($CH_3$), 121.3 ($C^4$), 125.4 (2C), 127.3 (2C), 127.9 (2C), 128.1, 128.2 (2C), 128.3, 128.9 (2C), 129.1, 129.1 (2C), 129.8, 130.4 (2C), 131.1 (2C), 131.6, 138.7, 139.7, 143.5, 145.5 and 152.3 ($C^3$, $C^5$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 450 (63) $[M]^+$, 385 (40), 295 (11) [$M$ – Ts], 293 (30), 267 (27) [$M$ – Ts – $N_2$], 189 (62), 180 (25), 91 (63), 77 (100), 65 (36), 51 (25). Found, %: C 74.59; H 4.87; N 6.15; S 7.18. $C_{28}H_{22}N_2O_2S$. Calculated, %: C 74.64; H 4.92; N 6.22; S 7.12. *M* 450.55.

**5-(Methanesulfonyl)-3,4,4-triphenyl-4*H*-pyrazole (6a).** Yield 0.30 g (80%), colorless crystals, mp 254–255°C (from $CH_2Cl_2$–petroleum ether; decomp.). IR spectrum, ν, cm$^{-1}$: 1497 m, 1331 m, 1311 v.s, 1138 m, 795 m, 768 m, 698 s. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.19 s (3H, $CH_3$), 7.30–7.33 m (4H, $H_{arom}$), 7.36–7.43 m (8H, $H_{arom}$), 7.47–7.52 m (1H, $H_{arom}$), 7.71–7.73 m (2H, $H_{arom}$). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: 43.4 ($CH_3$), 79.0 ($C^4$), 127.6, 128.3 (4C), 128.9 (2C), 129.2 (2C), 129.3 (2C), 129.4 (4C), 131.2, 132.6, 179.1, 180.5 ($C^3$, $C^5$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 374 (60) $[M]^+$, 373 (68), 295 (100) [$M$ – $SO_2CH_3$]$^+$, 294 (95), 267 (59) [$M$ – $SO_2CH_3$ – $N_2$]$^+$, 192 (55), 165 (95), 77 (65), 51 (37). Found, %: C 70.37; H 4.90; N 7.39; S 8.60. $C_{22}H_{18}N_2O_2S$. Calculated, %: C 70.57; H 4.85; N 7.48; S 8.56. *M* 374.46.

**5-(4-Methylbenzenesulfonyl)-3,4,4-triphenyl-4*H*-pyrazole (6b).** Yield 0.39 g (87%), colorless crystals, mp 191–192°C (from $CHCl_3$–petroleum ether). IR spectrum, ν, cm$^{-1}$: 1597 w, 1512 w, 1493 m, 1443 m, 1331 s, 1149 m, 760 s, 694 s, 671 s, 582 v.s. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s (3H, $CH_3$), 7.18 d (2H, $H_{arom}$, $J$ = 8.0 Hz), 7.23–7.26 m (2H, $H_{arom}$), 7.32–7.40 m (11H, $H_{arom}$), 7.49 d (2H, $H_{arom}$, $J$ = 8.2 Hz), 7.70 d (2H, $H_{arom}$, $J$ = 8.2 Hz). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 21.8 ($CH_3$), 80.0 ($C^4$), 128.5, 128.6 (2C), 128.8 (2C), 128.9 (4C), 129.2 (2C), 129.3 (4C), 129.7 (2C), 129.8 (2C), 131.7 (2C), 132.2, 136.4, 145.5, 180.9, 181.1 ($C^3$, $C^5$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 450 (15) $[M]^+$, 386 (20), 295 (14) [$M$ – Ts], 267 (525) [$M$ – Ts – $N_2$]$^+$, 192 (60), 180 (22), 165 (100), 91 (62), 77 (53), 65 (38), 51 (17). Found, %: C 74.49; H 4.85; N 6.08; S 7.04. $C_{28}H_{22}N_2O_2S$. Calculated, %: C 74.64; H 4.92; N 6.22; S 7.12. *M* 450.55.

**Transformations of 3*H*-pyrazoles 2a and 2b under microwave irradiation.** A microreactor was charged with a solution of 1 mmol of compound **2a** or **2b** in 35 mL of toluene, and the mixture was subjected to microwave irradiation for 40 min, maintaining the temperature at 180°C. The solvent was removed under reduced pressure (water-jet pump), and the solid residue was analyzed by $^1$H NMR. Crystalline indenes **15a** and **15b** were isolated by silica gel column chromatography.

**1-(Methanesulfonyl)-2,3-diphenyl-1*H*-indene (15a).** Yield 42%, light yellow crystals, mp 112–113°C. IR spectrum, ν, cm$^{-1}$: 3009 m, 2928 s, 1489 s, 1462 s, 1443 m, 1304 v.s, 1173 s, 1146 s, 1099 s, 768 s, 702 s. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.34 s (3H, $SO_2CH_3$), 5.41 s (1H, 1-H), 7.21–7.32 m (5H, $H_{arom}$), 7.32–7.45 m (8H, $H_{arom}$), 8.00 d (1H, $H_{arom}$, $J$ = 7.2 Hz). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 36.0 ($CH_3$), 73.5 ($C^1$), 121.4, 126.9, 128.0 (2C), 128.1, 128.2 (2C), 128.8 (2C), 129.1 (2C), 129.5, 129.8 (2C), 133.5, 133.6, 135.1, 136.1, 145.1, 145.4. Found, %: C 76.44; H 5.03; S 9.30. $C_{22}H_{18}O_2S$. Calculated, %: C 76.27; H 5.24; S 9.25.

**1-(4-Methylbenzenesulfonyl)-2,3-diphenyl-1*H*-indene (15b).** Yield 40%, colorless crystals, mp 129–130°C (from acetone–petroleum ether). IR spectrum, ν, $cm^{-1}$: 1316 s, 1169 s, 1080 m, 814 m, 771 m, 760 m, 694 m, 660 m, 575 v.s. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.36 s (3H, $CH_3$), 5.62 s (1H, 1-H), 6.77–6.79 m (2H, $H_{arom}$), 6.90 d (1H, $H_{arom}$, $J$ = 7.2 Hz), 6.99 d (2H, $H_{arom}$, $J$ = 8.1 Hz), 7.05 d (2H, $H_{arom}$, $J$ = 8.3 Hz), 7.10–7.13 m (2H, $H_{arom}$), 7.22–7.24 m (3H, $H_{arom}$), 7.27–7.33 m (4H, $H_{arom}$), 7.35–7.39 m (1H, $H_{arom}$), 8.11 d (2H, $H_{arom}$, $J$ = 7.4 Hz). $^{13}C$ NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 21.7 ($CH_3$), 74.0 ($C^4$), 120.8, 126.5, 126.9, 127.7, 127.9 (3C), 128.3 (2C), 128.7 (2C), 129.3, 129.4 (2C), 130.1 (2C), 132.0, 133.6, 134.2, 135.5, 135.6, 144.5, 145.1, 146.2 ($C^2$, $C^3$). Found, %: C 79.84; H 5.00; S 7.30. $C_{28}H_{22}O_2S$. Calculated, %: C 79.59; H 5.25; S 7.59.

**Photolysis of 3*H*-pyrazoles 3a and 3b (*general procedure*).** A quartz test tube was charged with a solution of 1 mmol of compound **3a** or **3b** in 20 mL of anhydrous methylene chloride, the test tube was tightly capped, and the solution was irradiated for 8–10 h with ultraviolet light using a DRT-400 lamp. The progress of the reaction was monitored by TLC. The solvent was removed under reduced pressure, and the residue was analyzed by $^1H$ NMR spectroscopy. Pure cyclopropenes **5a** and **5b** were isolated by column chromatography on silica gel.

**1-(Methanesulfonyl)-2,3,3-triphenylcyclopropene (5a).** Yield 67%, colorless crystals, mp 183–184°C (from $CH_2Cl_2$–petroleum ether). IR spectrum, ν, $cm^{-1}$: 2916 v.s, 1790 m, 1489 w, 1446 m, 1315 v.s, 1138 s, 960 m, 779 m, 764 s, 702 s, 690 m, 517 m. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.90 s (3H, $CH_3$), 7.26–7.29 m (2H, $H_{arom}$), 7.31–7.35 m (4H, $H_{arom}$), 7.40–7.43 m (4H, $H_{arom}$), 7.46–7.52 (3H, $H_{arom}$), 7.87–7.89 m (2H, $H_{arom}$). $^{13}C$ NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 44.4 ($CH_3$), 47.7 ($C^3$), 117.8, 124.2, 127.3 (2C), 128.3 (4S), 128.7 (4C), 129.4 (2C), 132.2 (2C), 132.5, 132.7, 141.9. Mass spectrum, $m/z$ ($I_{rel}$, %): 346 (0.2) $[M]^+$, 267 (100) [$M$ – $SO_2CH_3$], 251 (11), 238 (6), 189 (9), 165 (18). Found, %: C 76.00; H 5.12; S 9.23. $C_{22}H_{18}O_2S$. Calculated, %: C 76.27; H 5.24; S 9.25. $M$ 346.44.

**1-(4-Methylbenzenesulfonyl)-2,3,3-triphenylcyclopropene (5b).** Yield 71%, colorless crystals, mp 134–135°C (from $CH_2Cl_2$–petroleum ether). IR spectrum, ν, $cm^{-1}$: 1779 m (C=C), 1489 m, 1319 s, 1304 m, 1292 m, 1154 v.s, 1084 m, 721 s, 702 s, 683 s, 571 m, 544 s, 529 m. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.32 s (3H, $CH_3$), 7.07 d (2H, $H_{arom}$, $J$ = 8.1 Hz), 7.14–7.20 m (10H, $H_{arom}$), 7.40–7.51 m (3H, $H_{arom}$), 7.68 d (2H, $H_{arom}$, $J$ = 8.1 Hz), 7.76 d (2H, $H_{arom}$, $J$ = 7.3 Hz). $^{13}C$ NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 21.7 ($CH_3$), 47.7 ($C^3$), 119.1, 124.6, 126.7 (2C), 127.8 (2C), 128.25 (4C), 128.28 (4C), 129.3 (2C), 129.8 (2C), 131.6, 131.9 (2C), 132.1, 137.8, 141.5 (2C), 144.9. Found, %: C 79.48; H 5.13; S 7.39. $C_{28}H_{22}O_2S$. Calculated, %: C 79.59; H 5.25; S 7.59.

**Acid-catalyzed transformations of 3*H*-pyrazoles 2a, 2b, 3a, and 3b and 4*H*-pyrazoles 6a and 6b (*general procedure*).** Concentrated sulfuric acid, 0.1 mL, was added to a solution of 1 mmol of compound **2a**, **2b**, **3a**, **3b**, **6a**, or **6b** in 50 mL of glacial acetic acid, and the mixture was left to stand for 4–6 days at 20°C. The progress of the reaction was monitored by TLC. When the reaction was complete, the mixture was diluted with 250 mL of water, and the precipitate was filtered off and analyzed by $^1H$ NMR. Pyrazolone **16** was obtained from compounds **2** and **6**, and compounds **3a** and **3b** were converted into a mixture of 1*H*-pyrazole **17** and 22–25% of 1*H*-pyrazole **4a** or **4b**. Compounds **16** and **17** were isolated by crystallization from ethanol.

**3,4,4-Triphenyl-1*H*-pyrazol-5(4*H*)-one (16).** Yield 90% (from **2a**), 87% (from **6b**); colorless crystals, mp 164–165°C (from EtOH). IR spectrum, ν, $cm^{-1}$: 3213 w, 3063 w, 1709 v.s (C=O), 1497 w, 748 w, 694 w. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 7.22–7.43 m (13H, $H_{arom}$), 7.62 d (2H, $H_{arom}$, $J$ = 7.3 Hz), 9.76 br.s (1H, NH). $^{13}C$ NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 65.3 ($C^4$), 127.4 (2C), 128.3 (2C), 128.5 (2C), 129.0 (4C), 129.0 (4C), 130.0, 131.4, 136.4 (2C), 161.7 ($C^3$), 179.5 (C=O). Mass spectrum, $m/z$ ($I_{rel}$, %): 312 (100) $[M]^+$, 269 (79) [$M$ – HNCO], 252 (61), 194 (69) [$M$ – $C_6H_5CN_2H$], 180 (91), 166 (98), 165 (99), 152 (39), 139 (47), 77 (99), 51 (91). Found, %: C 80.47; H 5.13; N 8.68. $C_{21}H_{16}N_2O$. Calculated, %: C 80.75; H 5.16; N 8.97. $M$ 312.37.

**3,4,5-Triphenyl-1*H*-pyrazole (17).** Yield 0.13 g (44%, from **3a**), 0.12 g (41%, from **3b**); colorless crystals, mp 267–268°C (from EtOH); published data [28]: mp 265–266°C. IR spectrum, ν, $cm^{-1}$: 3217 w (NH), 1605 w, 1489 w, 1446 w, 1146 w, 972 w, 771 w, 729 m, 694 v.s, 605 w. $^1H$ NMR spectrum (DMSO-$d_6$), δ, ppm: 7.16–7.18 m (2H, $H_{arom}$), 7.27–7.35 m (13H, $H_{arom}$). $^{13}C$ NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: 116.8, 127.1, 127.4 (6C), 127.6, 128.4 (5C), 128.7 (3C), 130.6 (3C), 133.9. Mass spectrum, $m/z$ ($I_{rel}$, %): 296 (77) $[M]^+$, 295 (100), 218 (15), 189 (17), 165 (46),

104 (15), 89 (18), 77 (56), 51 (26). Found, %: C 85.02; H 5.50; N 9.39. $C_{21}H_{16}N_2$. Calculated, %: C 85.11; H 5.44; N 9.45. *M* 296.37.

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