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Synthesis of 3,3-Diphenyl-3*H*-pyrazoles Applying Vinyl Sulfones as Chemical Equivalents of Acetylenes in Reaction of 1,3-Dipolar Cycloaddition to Diphenyldiazomethane

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Abstract—Vinyl phenyl sulfone, methyl (*E*)-3-(phenylsulfonyl)- and methyl (*E*)-3-(*p*-tosyl)acrylates, (*E*)-3-(phenylsulfonyl)- and (*E*)-3-(*p*-tosyl)acrylonitriles react in ethyl ether at 20°C with diphenyldiazomethane leading to the formation of the corresponding 5,5-diphenyl-3-(arylsulfonyl)-Δ^2-pyrazolines. Products containing a methoxycarbonyl or cyano group at treating with DBU in dichloromethane at 0°C suffer a dehydrosulfonation and are converted into 4-substituted 3,3-diphenyl-3*H*-pyrazoles. The oxidation of the mentioned Δ^2-pyrazolines with activated manganese dioxide in benzene at 20°C leads to the formation of 4-methoxycarbonyl- and 4-cyano-substituted 5-arylsulfonyl-3,3-diphenyl-3*H*-pyrazoles respectively. The reactions of α-bromovinyl phenyl sulfones and α-bromovinyl methyl sulfones with diphenyldiazomethane afforded the corresponding 3-bromo-5,5-diphenyl-3-sulfonyl-Δ^1-pyrazolines. The first among them at 20°C suffered spontaneous elimination of molecular nitrogen and converted into 1-bromo-2,2-diphenyl-1-(phenylsulfonyl)cyclopropane whose structure was established by X-ray diffraction analysis. The action of DBU on another Δ^1-pyrazoline resulted in the formation of the product of the Ramberg–Bäcklund reaction, 5-methylene-3,3-diphenyl-Δ^1-pyrazoline together with the product of hydrodebromination–isomerization, 5,5-diphenyl-3-(methylsulfonyl)-Δ^2-pyrazoline.

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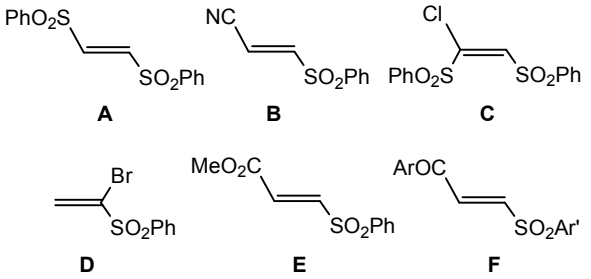
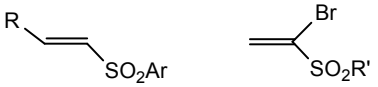
Some vinyl sulfones are known to be suitable synthetic equivalents of acetylene dienophiles in Diels–Alder reactions [1–5]. For instance, vinyl sulfones **A**–**C** were used as dienophiles in the reaction of concerted [4+2]-cycloaddition to cyclopentadiene, and the obtained cycloadducts were subjected in the first case to desulfonation, in the second case to dehydrosulfonation, and in the third case to dehydrochlorination resulting in norbornadiene [2], 2-cyanonorbornadiene [5], and 2,3-di(phenylsulfonyl)norbornadiene [4]. Thus the mentioned vinyl sulfones behaved in these Diels–Alder reactions as synthetic equivalents of acetylene proper, cyanoacetylene, and di(phenylsulfonyl)-acetylene respectively.

Numerous examples are also known of the utilization of vinyl sulfones as synthetic equivalents of acetylenes dipolarophiles in the reactions of concerted [3 + 2]-cycloaddition [6–8]. In particular, by the azomethine ylides cycloaddition to vinyl sulfones sulfonyl-substituted pyrrolidines were synthesized that at the treatment with bases (DBU, TMEDA, etc.) eliminated the arenesulfinic acid converting into dihydropyrroles. At the same time, in some cases managed to create dihydropyrroles that can not be obtained by cycloaddition reaction to the acetylenic dipolarophiles. Cycloadducts formed at azomethine ylides cycloaddition to sulfone **A** as a result of desulfonation underwent aromatization in pyrrole derivatives [9–12]. Pyrroles were also formed in a one-pot

process involving the azomethine ylides cycloaddition to bromovinyl sulfone **D** and the elimination of benzenesulfinic and hydrobromic acid under the treatment with DBU [13]. In these syntheses of substituted pyrroles vinyl sulfones **A** and **D** played the role of synthetic equivalents of acetylene. Similarly vinyl sulfone **E** was used as the equivalent of methyl propiolate in the 1,3-dipolar cycloaddition to pyrazolidinium ylides, and the yield of the target bicyclic pyrazolidinone turned out to be considerably higher than in its synthesis applying directly the acetylene dipolarophile [14]. The same procedure was utilized in the preparation of 3-aroyl-1*H*-pyrazole by the reaction of diazomethane in the presence of triethylamine with vinyl sulfone **F** playing the role of the synthetic equivalent of aroylacetylene [15].



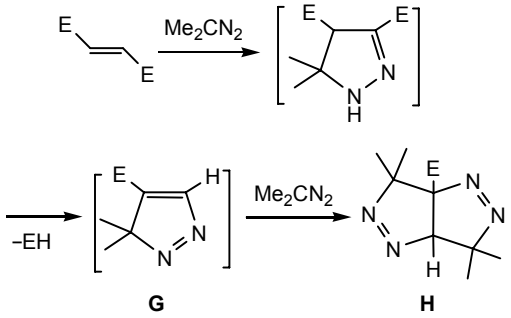
In this paper, we applied to the synthesis of derivatives of 3,3-diphenyl-3*H*-pyrazole underlain by the diphenyldi-azomethane cycloaddition to vinyl sulfones **1a**–**1c**, **2b**, **2c**, **3**, and **4** followed by the elimination of sulfinic or hydrobromic acids.



1a–**1c**, **2b**, **2c** **3**, **4**

R = H (**a**), CO_2Me (**b**), CN (**c**); Ar = Ph (**1**), *p*-Tol (**2**); R' = Me (**3**), Ph (**4**).

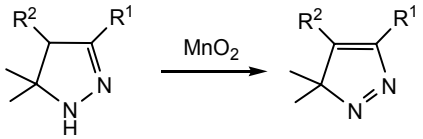
Our interest in this class of compounds was connected with our desire to extend the investigations of the van Alphen–Hüttel rearrangement [16, 17] to new objects aiming to reveal its general laws and to provide their better understanding. The main traditional preparation method for 3,3-disubstituted 3*H*-pyrazoles is the 1,3-dipolar cycloaddition of the disubstituted diazomethane to acetylene dipolarophile [18]. However the application of this method has some limitation thus promoting the search for new approaches to building up such systems. The only known synthesis attempt was described of the preparation of 3,3-disubstituted 3*H*-pyrazole by the cycloaddition of 2-diazopropane to (*E*)-1,2-di(arylsulfonyl)ethene used as a synthetic equivalent of arylsulfonylacetylene [19]. Yet the desired 3*H*-pyrazole **G** proved to be "elusive" and under the reaction conditions converted into bispyrazoline **H**.



G **H**

E = SO_2Ar.

Another approach to the synthesis of 3,3-disubstituted 3*H*-pyrazoles was attempted in [20] applying the oxidative dehydrogenation of the corresponding pyrazoline derivative which in its turn was obtained by the cycloaddition of 2-diazopropane to activated ethylenes, lacking, however, vinyl sulfones.

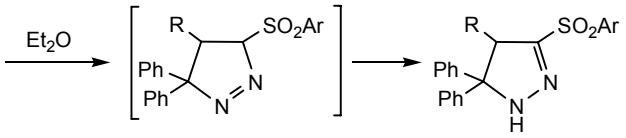


R^1 = NO_2, COMe, CO_2Me, CN; R^2 = Ph, CO_2Me, CN.

This approach we extended to the synthesis of sulfonyl-substituted 3,3-diphenyl-3*H*-pyrazoles.

Reactions of vinyl sulfones **1** and **2** with a slight excess of diphenyldiazomethane were carried out in anhydrous ethyl ether at 20°C within 20–60 h, and each reaction in 69–77% yield afforded a single product, Δ^2-pyrazolines **5** and **6**.

1a–**1c**, **2b**, **2c** + Ph_2CN_2



I **5a**–**5c**, **6b**, **6c**

Ar = Ph (**5**), *p*-Tol (**6**).

Δ^2-Pyrazolines **5a**–**5c**, **6b**, and **6c** were isolated in a crystalline state, and the presence of the appropriate

functional groups in the compounds was confirmed by the elemental analysis, IR, ^{1}H and ^{13}C NMR spectra. In particular, the presence of the NH group is shown in the ^{1}H NMR spectra by a broadened singlet at ~6.6–7.0 ppm, and in the IR spectra, by the absorption band in the region 3325–3417 cm^{-1} [21]. The observed regioselectivity of diphenyldiazomethane cycloaddition to vinyl sulfone **1a** appears to be evident, and therefore the structure of Δ^2-pyrazoline **5a** is doubtless. The structure of Δ^2-pyrazolines **5b**, **5c**, **6b**, and **6c** required additional confirmation. We applied to the study of the structure **6c** the method of long-range (multi-bond) correlations ^{1}H–^{13}C HMBC and H2BC [22]. A fragment of the HMBC spectrum of this compound is presented in Fig. 1. In the ^{1}H NMR spectrum atom H^4 appears as a signal at 5.79 ppm. This peak has three correlations in the HMBC spectrum with carbon signals at 82.16 (C^5), 115.17 (CN), and 141.45 (C^3) ppm, noted as ***a***, ***b***, and ***c*** respectively. The other cross-peaks correspond to the correlations in the aromatic fragments and are of no interest. It should be noted that this HMBC experiment does not provide an unambiguous answer of the structure of Δ^2-pyrazoline **6c** since it does not make it possible to distinguish the coupling constants $^2J_{H–C}$ and $^3J_{H–C}$ and decide between the structures **6c** and **6c'**.

A significant feature of HMBC spectrum should be stressed: The cross-peak ***a*** corresponds to the correlation between the quaternary atom C^5 and the atom H^4. The method H2BC which reveals only the CH-correlations through two bonds may be used additionally for the refining of the structure. This method is totally complementary to the HMBC method, but it does not indicate the correlations of the quaternary carbon atoms. A fragment of H2BC spectrum is shown in Fig. 2. In the spectrum two cross-peaks ***b′*** and ***c′*** are present corresponding to the couplings H^4–CN and H^4–C^3 respectively that provides a possibility to choose the structure **6c**.

The provided proof of the structure of pyrazoline **6c** makes it possible to extend the assignment of the structure not only to compound **5c**, but also to compounds **5b** and **6b**. The additional confirmation of the structure of pyrazoline **5b** is described further. Finally, the assumed structure of all Δ^2-pyrazolines **5** and **6** is confirmed by the presence of the signal at ~149 ppm in the ^{13}C NMR spectra that belongs to the atom C^3 linked to the sulfo group.

Therefore the regioselectivity of the cycloaddition of diphenyldiazomethane to vinyl sulfones **1b**, **1c**, **2b**, and **2c** turned out to be under a strict control of the sulfo group. We believe that the main cause of this control is the steric factor: The cyano and methoxycarbonyl groups are less bulky than the arylsulfonyl substituent.

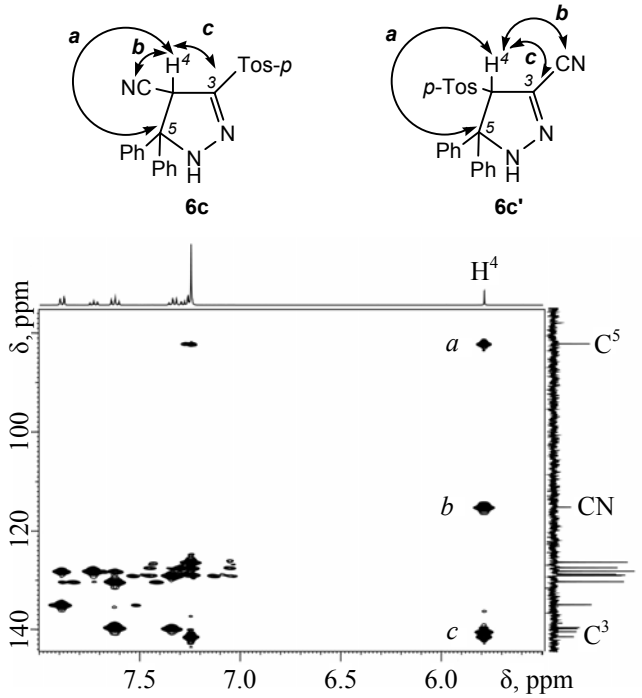


Fig. 1. Fragment of HMBC spectrum of 5,5-diphenyl-3-*p*-tosyl-Δ^2-pyrazoline-4-carbonitrile **6c**.

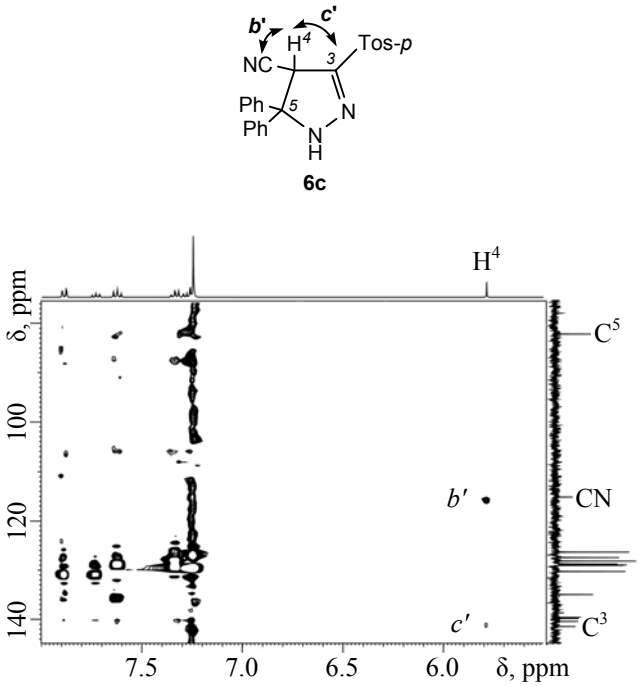
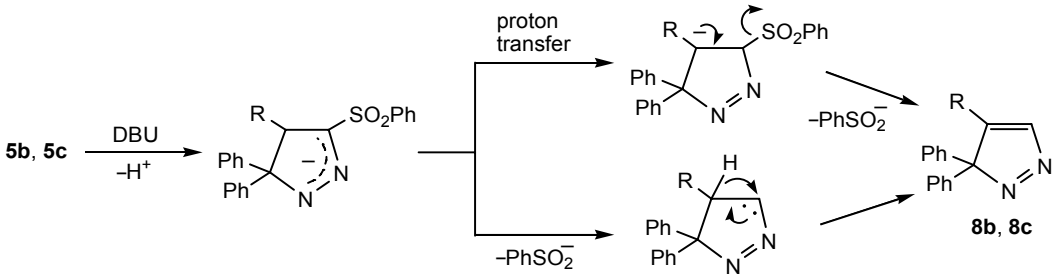
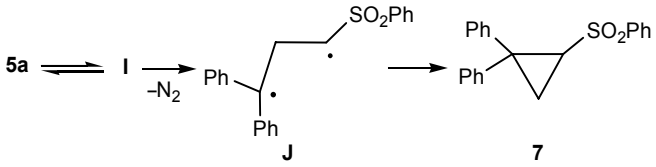


Fig. 2. Fragment of H2BC spectrum of 5,5-diphenyl-3-*p*-tosyl-Δ^2-pyrazoline-4-carbonitrile **6c**.



The formation of Δ^2-pyrazolines in analogous reactions of diazo compounds cycloaddition to activated alkenes is known to be a secondary process: The primarily formed Δ^1-pyrazoline **I** suffers a prototropic rearrangement. This rearrangement of compound **5a** is likely to be reversible since at boiling in benzene for 12 h it completely converts into cyclopropane **7** via biradical **J** as a result of nitrogen elimination; the latter process is possible only with Δ^1-pyrazoline. At the same time compound **6c** proved to be stable against boiling in benzene for 50 h. The structure of cyclopropane **7** is confirmed by spectral characteristics.

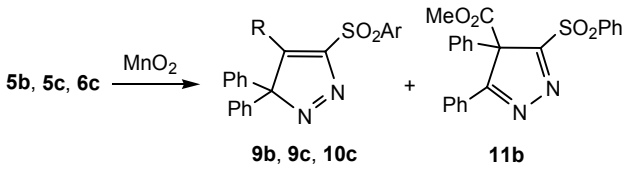


Further we turned to the study of the dehydrosulfonation of Δ^2-pyrazoline **5b** and **5c** in order to prepare the corresponding 3*H*-pyrazoles. At their treatment with the 1,5-fold DBU excess in dichloromethane at 0°C compounds **8b** and **8c** formed in 61–72% yields. In contrast, Δ^2-pyrazoline **5a** at this treatment remains unchanged.

The possible mechanism includes a deprotonation stage. Then in the arising anion a proton transfer is probable from the adjacent acid site followed by the elimination of the phenylsulfinate anion. An alternative route is also possible: A carbene formation with a subsequent 1,2-hydride shift. The first route is supported as we presume by the stability under the chosen conditions against the dehydrosulfonation of pyrazoline **5a** lacking an additional activating group.

The structure of 3*H*-pyrazoles **8b** and **8c** is confirmed by the IR, ^{1}H and ^{13}C NMR spectra. In their ^{1}H NMR spectra the singlet signal of H^5 at ~8.1 ppm is characteristic. The spectral characteristics of 3*H*-pyrazole **8b** essentially differ from the characteristics of its known [23] regioisomer, 3,3-diphenyl-5-methoxycarbonyl-3*H*-pyrazol **8b'**, cycloadduct of methyl propiolate to diphenyldiazomethane. We proved it by reproducing the synthesis of the latter. This synthesis proved both the structure of compound **8b** and of its precursor, pyrazoline **5b**.

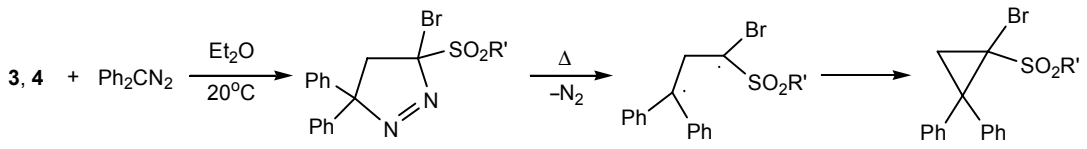
After that we carried out the dehydrogenation of pyrazolines **5b**, **5c**, and **6c** by oxidation with activated manganese dioxide [20, 24]. The reaction was performed at 20°C while stirring the reagents solutions in a mixture benzene–dichloromethane, 1 : 1, for 20 h in the presence of 12-fold molar excess of MnO_2. We obtained from compound **5b** 3*H*-pyrazole **9b** with the admixture of 4*H*-pyrazole **11b**. Compounds **5c** and **6c** were completely converted into 3*H*-pyrazoles **9c** and **10c**. Pyrazoline **5a** was not oxidized with MnO_2 as had been observed before [20] for related (but not sulfonyl-containing) 2-pyrazolines with the unsubstituted position *4*.



Ar = Ph (**9**), *p*-Tol (**10**).

3*H*-Pyrazoles **9c** and **10c** were isolated in the crystalline state. We failed to isolate compound **9b**, and it was characterized in the presence of 4*H*-pyrazole **11b** using ^{1}H NMR spectra applying the DOSY-experiment. The structure of pyrazoles **9c**, **10c**, and **11b** was confirmed by IR, ^{1}H and ^{13}C NMR spectra taking into account the data for related compounds [25, 26]. 4*H*-Pyrazole **11b** is the product of the thermal van Alphen–Hüttel rearrangements of 3*H*-pyrazole **9b**. The rearrangement can be clearly observed already at room temperature and is completed within 10 min at boiling in toluene.

The successful synthesis of 3*H*-pyrazoles **9b**, **9c**, and **10c** allows regarding vinyl sulfones **5b**, **5c**, and **6b**



R' = Me (**12**, **14**), Ph (**13**, **15**).

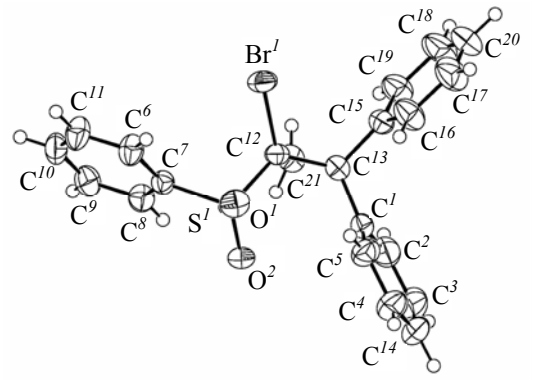


Fig. 3. Perspective view of the molecule of 1-bromo-2,2-diphenyl-1-(phenylsulfonyl)cyclopropane **14** according to XRD data.

as convenient chemical equivalents of difficultly accessible and unstable esters and nitriles of sulfonyl-substituted acetylenecarboxylic acid.

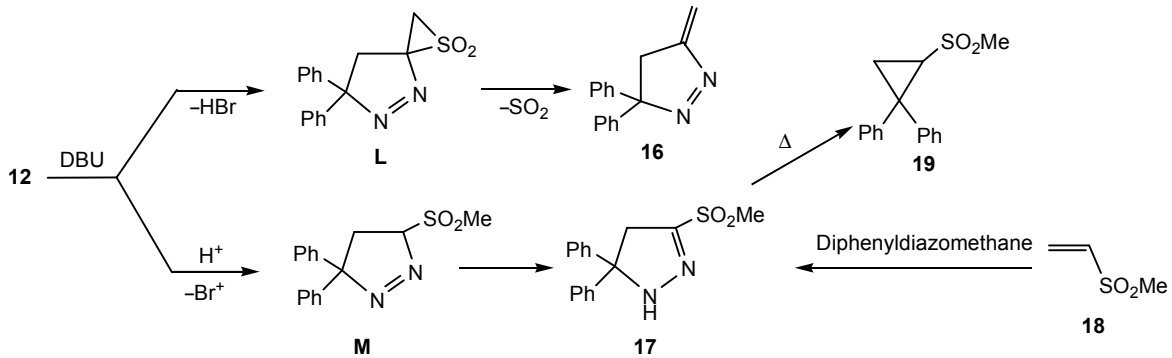
Finally, we investigated the possibility to synthesize 3*H*-pyrazoles applying bromovinyl sulfones **3** and **4** as synthetic equivalents of sulfonylacetylene. To this end by the reactions between these compounds and diphenyldiazomethane we obtained Δ^1-pyrazolines **12** and **13**.

The pyrazolines were isolated in a crystalline state and characterized by IR, ^{1}H and ^{13}C NMR spectra. The regiochemistry of the cycloaddition is here undoubtless. Δ^1-Pyrazoline **13** turned out to be thermally unstable compound, whose notable nitrogen elimination with the formation of cyclopropane **15** was observed already at room temperature. Pyrazoline **12** is more stable against heating, but both pyrazolines **12** and **13** at short boiling (10–20 min) in toluene afforded in a high yield cyclopropanes **14** and **15** respectively. The nitrogen elimination occurs obviously through the intermediate biradicals **K**. The structure of compounds **12–15** was established with the help of ^{1}H and ^{13}C spectroscopy, mass spectrometry, and was confirmed by the elemental analysis data. Besides compound **14** was subjected to XRD analysis (Fig. 3).

Our attempt to carry out dehydrobromination of pyrazoline **13** by treating with DBU in CH_2Cl_2 at 0–20°C aiming at the preparation of the corresponding 3*H*-pyrazole derivative failed: Only cyclopropane **15** was obtained.

Δ^1-Pyrazoline **12** at treating with DBU in CH_2Cl_2 at 0–20°C gave a mixture of two compounds **16** and **17** in a ratio 0.6 : 1. 5-Methylene-Δ^1-pyrazoline **16** is a product of Ramberg–Bäcklund reaction [27] that includes the 1,3-dehydrobromination giving episulfone **L** and the thermal decomposition of the latter with sulfur dioxide elimination (cf. [28]). 5,5-Diphenyl-3-(methylsulfonyl)-Δ^2-pyrazoline **17** forms involving a base in the halophilic hydrodebromination reaction through the intermediate Δ^1-pyrazoline **M**.

The structure of compounds **16** and **17** isolated in an individual state by flash-chromatography on silica gel was confirmed by IR, ^{1}H and ^{13}C NMR spectra. Besides Δ^2-pyrazoline **17** was prepared by an authentic



synthesis in a reaction of vinyl methyl sulfone **18** with diphenyldiazomethane. In the formation of methylene-pyrazoline **16** vinyl sulfone **12** acts as a synthetic equivalent of unsubstituted allene.

Pyrazoline **17**, like its analog **5a**, was not oxidized by activated MnO_2 into the corresponding 3*H*-pyrazole. On the other hand, pyrazoline **17** proved to be prone to thermal nitrogen elimination as its analog **5a**: as a result of the reaction cyclopropane **19** was obtained.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on a spectrometer ECX-400 JEOL (399.8 and 100.5 MHz respectively) from solutions of compounds in $CDCl_3$. The correlation HMBC (Δ 62.5 ms) and H2BC (*T* 22 ms) spectra were taken in DMSO-d_6 using thermal stabilization at 30°C and a low-pass *J*-filter of III order in the range $120 < {}^1J < 160$ Hz applying pulse field gradient. Matrix size 819, 256, points number 1024, 128, relaxation delay 2.54 s. Compound **9b** in the mixture with 4*H*-pyrazole **11b**, 1.6 : 1, was characterized applying the diffusion-ordered ^{1}H NMR spectroscopy (DOSY) [29, 30] using a bipolar pulse sequence BPP LED [31] at 298 K. The amplitude of field gradient was varied from 20 to 280 mT/m (logarithmic function of base 2) for 10 points. The data acquisition was performed with parameters Δ 70 ms, δ 1 ms, T_e 50 ms, relaxation delay 7 s, data array 8 × 1024 points. The results were processed by the procedure SPLMOD [32] (10^{-10}–10^{-8} m^2/s, 15 points, 3 components including $CDCl_3$).

IR spectra were recorded on a Fourier spectrophotometer InfraLYuM FT-02 from pellets with KBr. Elemental analyses were carried out on a CHNS-analyzer VarioMICRO. Mass spectra were taken using the system KONIK RBK-HRGC5000B-MSQ12, EI, 70 eV. Analytic TLC was performed on Sorbfil plates, eluent light petroleum ether–acetone, 4 : 1, development in iodine vapor. The flash-chromatography on a dry column was carried out applying silica gel L 5/40, eluent light petroleum ether–ethyl acetate 4–1 : 1. Melting points of compounds were measured in sealed glass capillaries using melting point analyzer MP-50 (Mettler Toledo, Switzerland).

Vinyl phenyl sulfone **1a** [33], (*E*)-3-(*p*-tosyl) acrylonitrile **2c** [34], α-bromovinyl sulfones **3** [35], **4** [36], vinyl methyl sulfone **18** [35], and diphenyldiazomethane [37] were obtained by published methods. Methyl (*E*)-3-(phenylsulfonyl)acrylate **1b**, mp 95–96°C (98–99°C [38], 97°C [39]), methyl (*E*)-3-(*p*-tosyl)acrylate **2b**, mp 116–117°C (117°C [39]), and (*E*)-3-(phenylsulfonyl)acrylonitrile **1c**, mp 103°C (103–104°C [37]) were prepared by arylsulfo-iodination–dehydroiodination of methyl acrylate and acrylonitrile by procedure [34].

Reactions of compounds (1a–1c, 2b, and 2c) with diphenyldiazomethane. To a solution of 8 mmol of vinyl sulfone **1a–1c**, **2b**, and **2c** in 35 mL of anhydrous ethyl ether was added a solution of 1.55 g (8 mmol) of diphenyldiazomethane in the same volume of this solvent. The reaction mixture was kept at 20°C in a tightly stoppered flask away from light for 20–60 h till the disappearance of the red-purple color of the initial diazo compound. The precipitated crystals of Δ^2-pyrazoline **5a–5c**, **6b**, and **6c** were filtered off and washed with ethyl ether.

5,5-Diphenyl-3-(phenylsulfonyl)-Δ^2-pyrazoline (5a). Yield 77%. Light-yellow crystals, mp 146–147°C. IR spectrum, ν, cm^{-1}: 3325 s (NH), 1547 m, 1447 s, 1396 m, 1319 s (asymm. SO_2), 1180 m, 1146 v.s (symm. SO_2), 1076 m, 760 m, 721 s, 687 s, 606 v.s, 563 m, 532 m. ^{1}H NMR spectrum, δ, ppm: 3.58 s (2H, H^4), 6.60 br.s (1H, NH), 7.11–7.17 m (4H$_{arom}$), 7.24–7.31 m (6H$_{arom}$), 7.55 t (2H$_{arom}$, *J* 7.8 Hz), 7.65 t (1H$_{arom}$, *J* 7.3 Hz), 7.97 d (2H$_{arom}$, *J* 7.9 Hz). ^{13}C NMR spectrum, δ, ppm: 43.8 (C^4), 77.5 (C^5), 126.1 (4C$_{arom}$), 127.8 (2C$_{arom}$), 128.3 (2C$_{arom}$), 128.4 (4C$_{arom}$), 129.3 (2C$_{arom}$), 134.0 (2C$_{arom}$), 138.6 w (2C$_{arom}$), 143.9 w (1C$_{arom}$), 149.2 (C^3). Found, %: C 69.76; H 4.94; N 7.76; S 8.86. $C_{21}H_{18}N_2O_2S$. Calculated, %: C 69.59; H 5.01; N 7.73; S 8.85.

Methyl 5,5-diphenyl-3-(phenylsulfonyl)-Δ^2-pyrazoline-4-carboxylate (5b). Yield 69%. Light-yellow crystals, mp 206–207°C. IR spectrum, ν, cm^{-1}: 3341 m (NH), 1732 v.s (C=O), 1555 w, 1493 w, 1446 m, 1319 s (asymm. SO_2), 1269 m, 1138 m (symm. SO_2), 1080 w, 856 w, 752 m, 687 m, 606 m, 536 m. ^{1}H NMR spectrum, δ, ppm: 2.97 s (3H, OCH_3), 4.86 s (1H, H^4), 6.64 s (1H, NH), 7.07–7.13 m (2H$_{arom}$), 7.23–7.33 m (8H$_{arom}$), 7.53–7.59 m (2H$_{arom}$), 7.63–7.67 m (1H$_{arom}$), 7.99–8.02 m (2H$_{arom}$). ^{13}C NMR spectrum, δ, ppm: 52.0 (OCH_3), 58.6 (C^4), 81.3 (C^5), 125.7 (2C$_{arom}$), 127.9 (2C$_{arom}$), 128.1 (2C$_{arom}$), 128.2 (1C$_{arom}$), 128.5 (2C$_{arom}$), 128.6 (1C$_{arom}$), 129.0 (2C$_{arom}$), 129.2 (2C$_{arom}$), 134.0 (1C$_{arom}$), 138.7 w (1C$_{arom}$), 139.0 w (1C$_{arom}$), 143.5 w (1C$_{arom}$), 147.0 (C^3), 166.8 (C=O). Found, %:

C 65.77; H 4.74; N 6.69; S 7.68. $C_{23}H_{20}N_2O_4S$. Calculated, %: C 65.70; H 4.79; N 6.66; S 7.62.

5,5-Diphenyl-3-(phenylsulfonyl)-Δ²-pyrazoline-4-carbonitrile (5c). Yield 72%. Light-yellow crystals, mp 195–196°C. IR spectrum, ν, cm^{-1}: 3417 w (NH), 2927 w, 1489 w, 1462 m, 1442 w, 1303 v.s (asymm. SO_2), 1172 m, 1145 m (symm. SO_2), 1099 m, 945 w, 837 w, 767 m, 702 m, 625 w, 544 m, 517 m. ^1H NMR spectrum, δ, ppm: 4.96 s (1H, H^4), 7.03 s (1H, NH), 7.15–7.22 m ($4H_{arom}$), 7.28–7.34 m ($3H_{arom}$), 7.36–7.40 m ($3H_{arom}$), 7.59 t ($2H_{arom}$, *J* 7.9 Hz), 7.69 t ($1H_{arom}$, *J* 7.3 Hz), 8.07 d ($2H_{arom}$, *J* 7.5 Hz). ^{13}C NMR spectrum, δ, ppm: 45.1 (C^5), 81.8 (C^4), 112.8 (CN), 125.8 ($2C_{arom}$), 127.3 ($2C_{arom}$), 128.6 ($1C_{arom}$), 128.8 ($2C_{arom}$), 129.1 ($1C_{arom}$), 129.3 ($4C_{arom}$), 129.5 ($2C_{arom}$), 134.6 w ($1C_{arom}$), 138.5 w ($1C_{arom}$), 138.6 w ($1C_{arom}$), 141.1 w ($1C_{arom}$), 142.8 (C^3). Found, %: C 68.27; H 4.40; N 10.96; S 8.16. $C_{22}H_{17}N_3O_2S$. Calculated, %: C 68.20; H 4.42; N 10.85; S 8.27.

Methyl-5,5-diphenyl-3-*p*-tosyl-Δ²-pyrazoline-4-carboxylate (6b). Yield 66%. Light-yellow crystals, mp 104–105°C. IR spectrum, ν, cm^{-1}: 3314 m (NH), 3009 w, 2952 w, 1740 v.s (C=O), 1327 s (asymm. SO_2), 1304 m, 1250 m, 1150 m (symm. SO_2), 1119 m, 1076 m, 1022 m, 749 m, 706 m, 664 m, 594 m, 544 m. ^1H NMR spectrum, δ, ppm: 2.44 s (3H, CH_3), 3.00 s (3H, OCH_3), 4.25 s (1H, H^4), 7.10 d ($2H_{arom}$, *J* 7.5 Hz), 7.14–7.21 m ($1H_{arom}$), 7.25–7.30 m ($7H_{arom}$, NH), 7.35 d ($2H_{arom}$, *J* 8.1 Hz), 7.75–7.83 m ($1H_{arom}$), 7.87 d ($2H_{arom}$, *J* 8.1 Hz). ^{13}C NMR spectrum, δ, ppm: 21.7 (CH_3), 51.9 (OCH_3), 58.5 (C^3), 81.1 (C^4), 125.7 ($2C_{arom}$), 127.9 ($2C_{arom}$), 128.08 ($2C_{arom}$), 128.14 ($1C_{arom}$), 128.55 (C_{arom}), 128.60 ($2C_{arom}$), 128.9 ($2C_{arom}$), 129.8 ($2C_{arom}$), 135.9 ($1C_{arom}$), 138.7 ($1C_{arom}$), 143.6 w ($1C_{arom}$), 145.1 w ($1C_{arom}$), 147.3 (C^5), 166.9 (C=O). Found, %: C 66.36; H 5.24; N 6.56; S 7.28. $C_{24}H_{22}N_2O_4S$. Calculated, %: C 66.34; H 5.10; N 6.45; S 7.38.

5,5-Diphenyl-3-*p*-tosyl-Δ²-pyrazoline-4-carbonitrile (6c). Yield 56%. Light-yellow crystals, mp 159–160°C. IR spectrum, ν, cm^{-1}: 3345 m (NH), 2952 m, 2253 w (CN), 1593 m, 1559 s, 1493 m, 1447 m, 1385 m, 1335 s (asymm. SO_2), 1296 m, 1188 s, 1161 v.s (symm. SO_2), 1076 m, 1019 m, 999 m, 872 m, 845 m, 822 m, 768 s, 702 s, 668 s, 652 s, 583 v.s, 556 s, 521 v.s, 490 s. ^1H NMR spectrum, δ, ppm: 2.44 s (3H, CH_3), 4.93 s (1H, H^4), 7.00 s (1H, NH), 7.17–7.21 m ($4H_{arom}$), 7.28–7.33 m ($3H_{arom}$), 7.36–7.38 m ($5H_{arom}$), 7.93 d ($2H_{arom}$, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 21.8 (CH_3), 45.0 (C^4), 81.7 (C^5), 112.8 (CN), 125.8 ($2C_{arom}$), 127.3 ($2C_{arom}$), 128.6 ($2C_{arom}$), 128.8 ($2C_{arom}$), 129.0 ($1C_{arom}$), 129.2 ($3C_{arom}$), 130.2 ($2C_{arom}$), 135.2 ($1C_{arom}$), 138.6 w ($1C_{arom}$), 141.1 w ($1C_{arom}$), 142.9 w ($1C_{arom}$), 145.9 (C^5). Found, %: C 68.76; H 4.49; N 10.46; S 7.96. $C_{23}H_{19}N_3O_2S$. Calculated, %: C 68.81; H 4.77; N 10.47; S 7.99.

1-Phenylsulfonyl-2,2-diphenylcyclopropane (7). 400 mg (1.1 mmol) of Δ²-pyrazoline **5a** was boiled in 6 mL of anhydrous benzene for 12 h. After the removal of the solvent on the rotary evaporator the solid residue was crystallized. Yield 235 mg (64%), mp 119–120°C (benzene). IR spectrum, ν, cm^{-1}: 3056 w, 3036 w, 1497 m, 1447 s, 1308 v.s (asymm. SO_2), 1289 m, 1154 v.s, 1146 v.s (symm. SO_2), 1088 m, 768 s, 745 s, 706 s, 698 s, 586 s, 571 m, 540 m. ^1H NMR spectrum, δ, ppm: 1.78 d.d (1H, H^3, *J* 5.6, 8.7 Hz), 2.50 d.d (1H, H^3, *J* 5.8, 8.7 Hz), 3.25 d.d (1H, H^1, *J* 5.6, 5.8 Hz), 7.17–7.25 m ($8H_{arom}$), 7.32–7.35 m ($2H_{arom}$), 7.47 t ($2H_{arom}$, *J* 7.6 Hz), 7.59 t ($1H_{arom}$, *J* 7.3 Hz), 7.69 d ($2H_{arom}$, *J* 7.3 Hz). ^{13}C NMR spectrum, δ, ppm: 18.7 (C^3), 40.6 (C^2), 45.5 (C^1), 127.1 ($1C_{arom}$), 127.4 ($1C_{arom}$), 127.6 ($2C_{arom}$), 127.8 ($2C_{arom}$), 128.1 ($2C_{arom}$), 128.7 ($2C_{arom}$), 129.0 ($2C_{arom}$), 129.9 ($2C_{arom}$), 133.2 ($1C_{arom}$), 136.9 w ($1C_{arom}$), 140.9 w ($1C_{arom}$), 143.7 w ($1C_{arom}$). Found, %: C 75.46; H 3.41; S 9.48. $C_{21}H_{18}O_2S$. Calculated, %: C 75.42; H 3.47; S 9.59.

Dehydrosulfonation of Δ²-pyrazolines (5b and 5c). **General procedure**. To a solution of 1.29 mmol of compound **5b** and **5c** in 20 mL of anhydrous CH_2Cl_2 at stirring in inert atmosphere while cooling to 0°C was added dropwise 1.55 mmol of DBU. The reaction mixture was stirred at the same temperature for 1.5 h (TLC monitoring). Then the mixture was filtered through a silica gel bed (1 cm). The solvent was evaporated in a vacuum of the water-jet pump. The reaction product was isolated from the residue by flash-chromatography.

Methyl 3,3-diphenyl-3*H*-pyrazole-4-carboxylate (8b). Yield 72%, yellow oil. IR spectrum, ν, cm^{-1}: 3060 w, 2952 w, 1725 v.s (C=O), 1493 m, 1447 m, 1239 s, 1127 m, 1011 m, 772 m, 749 m, 698 s. ^1H NMR spectrum, δ, ppm: 3.78 s (3H, OCH_3), 7.19–7.23 m ($4H_{arom}$), 7.31–7.35 m ($6H_{arom}$), 8.12 s (1H, H^5). ^{13}C NMR spectrum, δ, ppm: 52.4 (OCH_3), 106.2 (C^3), 128.5 ($8C_{arom}$), 128.6 (C^5), 134.3 w ($2C_{arom}$), 148.0 ($2C_{arom}$), 148.2 (C^4), 161.7 (C=O). Found, %: C 73.28; H 5.91; N 10.12. $C_{17}H_{14}N_2O_2$. Calculated, %: C 73.37; H 5.07; N 10.07.

3,3-Diphenyl-3*H*-pyrazole-4-carbonitrile (8c). Yield 61%, colorless crystals, mp 66–67°C. IR spectrum, ν, cm^{-1}: 3063 w, 2230 w (CN), 1489 m, 1447 s, 926 m, 764 m, 756 s, 698 v.s, 660 m. ^1H NMR spectrum, δ, ppm: 7.28–7.32 m ($4H_{arom}$), 7.33–7.36 m ($6H_{arom}$), 8.05 s (1H, H^5). ^{13}C NMR spectrum, δ, ppm: 108.4 (C^3), 112.6 (CN), 127.5 ($4C_{arom}$), 129.1 ($4C_{arom}$), 129.3 ($2C_{arom}$), 130.4 (C^5), 133.7 w ($2C_{arom}$), 149.4 (C^4). Found, %: C 78.38; H 4.61; N 17.20. $C_{16}H_{11}N_3$. Calculated, %: C 78.35; H 4.52; N 17.13.

Methyl-3,3-diphenyl-3*H*-pyrazole-5-carboxylate (8'b). A solution of 0.5 g (6 mmol) of methyl propiolate in 50 mL of anhydrous ethyl ether was mixed with 1.27 g (6.5 mmol) of diphenyldiazomethane, and the mixture was kept for 1 h at 20°C. Precipitated crystals were filtered off and dried in air. Yield 0.9 g (54%), mp 139–140°C (decomp.). IR spectrum, ν, cm^{-1}: 3093 m, 1740 v.s (C=O), 1450 m, 1300 s, 1099 m, 698 s. ^1H NMR spectrum, δ, ppm: 3.99 s (3H, OCH_3), 7.27–7.36 m ($10H_{arom}$), 8.22 s (1H, H^4). ^{13}C NMR spectrum, δ, ppm: 55.8 (OCH_3), 107.3 (C^3), 127.9 ($4C_{arom}$), 128.9 ($2C_{arom}$), 129.1 ($4C_{arom}$), 135.2 (C^4), 147.7 (C^5), 151.9 ($2C_{arom}$), 161.2 (C=O). Found, %: C 73.38; H 5.21; N 10.01. $C_{17}H_{14}N_2O_2$. Calculated, %: C 73.37; H 5.07; N 10.07.

Oxidative dehydrogenation of Δ^2-pyrazolines (5b, 5c, and 6c). **General procedure**. To a solution of 1.5 mmol of Δ^2-pyrazoline **5b**, **5c**, and **6c** in a mixture of 20 mL of anhydrous benzene and 20 mL of dry CH_2Cl_2 was added 1.63 g (18.7 mmol) of activated MnO_2 [31]. The mixture was stirred at 20°C for 20 h, then it was filtered. The filtrate was evaporated on a rotary evaporator, and the residue was analyzed by NMR spectroscopy. From pyrazoline **5b** we obtained a mixture of 3*H*- and 4*H*-pyrazoles **9b** and **11b** in a ratio 1.6 : 1 in an overall yield 67%, which we did not succeed to separate. In the reaction products of cyano-substituted derivatives **5c** and **6c** only 3*H*-pyrazoles **9c** and **10c** were present.

Methyl 3,3-diphenyl-5-(phenylsulfonyl)-3*H*-pyrazole-4-carboxylate (9b). ^1H NMR spectrum (from DOSY-experiment), δ, ppm: 3.84 s (3H, OCH_3), 7.12 d ($4H_{arom}$, *J* 7.1 Hz), 7.28–7.41 m ($6H_{arom}$), 7.61 t ($2H_{arom}$, *J* 7.8 Hz), 7.71 t ($1H_{arom}$, *J* 7.3 Hz), 8.16 d ($2H_{arom}$, *J* 7.4 Hz).

3,3-Diphenyl-5-(phenylsulfonyl)-3*H*-pyrazole-4-carbonitrile (9c). Yield 58%, bright yellow crystals, mp 103–104°C. IR spectrum, ν, cm^{-1}: 2248 w (CN), 1447 m, 1354 s (asymm. SO_2), 1157 s (symm. SO_2), 1088 m, 756 v.s, 733 s, 687 s, 660 m, 648 m, 590 s, 556 m. ^1H NMR spectrum, δ, ppm: 7.19 d ($4H_{arom}$, *J* 7.9 Hz), 7.34–7.43 m ($6H_{arom}$), 7.66 t ($2H_{arom}$, *J* 7.5 Hz), 7.78 t ($1H_{arom}$, *J* 7.2 Hz), 8.22 d ($2H_{arom}$, *J* 8.1 Hz). ^{13}C NMR spectrum, δ, ppm: 110.3 (C^3), 111.4 (CN), 127.6 ($4C_{arom}$), 129.3 ($2C_{arom}$), 129.6 ($4C_{arom}$), 130.0 ($2C_{arom}$), 130.1 w ($2C_{arom}$), 132.1 w. ($1C_{arom}$), 132.3 ($1C_{arom}$), 135.7 w ($2C_{arom}$), 136.9 (C^4), 158.8 (C^5). Found, %: C 68.51; H 3.91; N 10.93; S 8.26. $C_{22}H_{15}N_3O_2S$. Calculated, %: C 68.56; H 3.92; N 10.90; S 8.32.

3,3-Diphenyl-5-*p*-tosyl-3*H*-pyrazole-4-carbonitrile (10c). Yield 76%, bright yellow crystals, mp 57–58°C. IR spectrum, ν, cm^{-1}: 2215 w (CN), 1593 m, 1447 m, 1354 s (asymm. SO_2), 1157 v.s (symm. SO_2), 1084 m, 710 s, 695 m, 664 m, 590 s, 536 m. ^1H NMR spectrum, δ, ppm: 2.48 s (3H, CH_3), 7.19 d ($4H_{arom}$, *J* 7.8 Hz), 7.34–7.41 m ($6H_{arom}$), 7.44 d ($2H_{arom}$, *J* 8.1 Hz), 8.09 d ($2H_{arom}$, *J* 8.1 Hz). ^{13}C NMR spectrum, δ, ppm: 21.9 (CH_3), 110.3 (C^3), 111.2 (CN), 127.6 ($4C_{arom}$), 129.4 ($2C_{arom}$), 129.5 ($4C_{arom}$), 130.0 ($2C_{arom}$), 130.6 ($2C_{arom}$), 131.5 w ($1C_{arom}$), 132.3 ($2C_{arom}$), 133.8 (C^4), 147.4 ($1C_{arom}$), 159.5 (C^5). Found, %: C 69.18; H 4.31; N 10.53; S 8.06. $C_{23}H_{17}N_3O_2S$. Calculated, %: C 69.16; H 4.29; N 10.52; S 8.03.

Methyl-3,4-diphenyl-5-(phenylsulfonyl)-4*H*-pyrazole-4-carboxylate (11b). A solution of 0.21 g (0.5 mmol) of a mixture of compounds **9b** and **11b**, 0.9 : 1, in 10 mL of anhydrous toluene was boiled in an argon atmosphere for 10 min. The solvent was removed on a rotary evaporator to get 0.18 g (88%) of 4*H*-pyrazole **11b**. Colorless crystals, mp 35–36°C. IR spectrum, ν, cm^{-1}: 3067 w, 1752 v.s (C=O), 1509 m, 1493 m, 1443 m, 1343 s (asymm. SO_2), 1231 s, 1200 m, 1184 m, 1153 s (symm. SO_2), 1080 m, 756 m, 725 s, 687 s, 610 s, 571 m, 529 m. ^1H NMR spectrum, δ, ppm: 3.80 s (3H, OCH_3), 7.23–7.28 m ($4H_{arom}$), 7.31–7.37 m ($5H_{arom}$), 7.46 t ($1H_{arom}$, *J* 7.3 Hz), 7.52 t ($1H_{arom}$, *J* 8.2 Hz), 7.59 d ($2H_{arom}$, *J* 7.2 Hz), 7.92 d ($2H_{arom}$, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 54.0 (OMe), 78.0 (C^4), 126.9 w ($1C_{arom}$), 128.3 ($2C_{arom}$), 128.47 ($2C_{arom}$), 128.54 w. ($1C_{arom}$), 128.8 ($2C_{arom}$), 128.9 ($2C_{arom}$), 129.2 ($2C_{arom}$), 129.4 ($1C_{arom}$), 129.9 ($2C_{arom}$), 133.0 ($1C_{arom}$), 134.2 ($1C_{arom}$), 138.5 w ($1C_{arom}$), 164.4 (C=O), 174.7 (C^3), 177.4 (C^5). Found, %: C 66.11; H 4.21; N 6.62; S 7.60. $C_{23}H_{18}N_2O_4S$. Calculated, %: C 66.02; H 4.34; N 6.69; S 7.66.

Reaction of α-bromovinylsulfones (3 and 4) with diphenyldiazomethane. To a solution of 8.10 mmol of sulfone **3** or **4** in 25 mL of anhydrous ethyl ether

was added a solution of 1.73 g (8.92 mmol) of diphenyldiazomethane in 10 mL of the same solvent. The reaction mixture was kept at 20°C in a place protected from light for 8 h. The precipitated colorless crystals were filtered off and washed on the filter with 10 mL of ethyl ether.

3-Bromo-5,5-diphenyl-3-(methylsulfonyl)-Δ^1-pyrazoline (12). Yield 83%, mp 115–116°C (decomp.). IR spectrum, ν, cm^{-1}: 1447 m, 1327 v.s (asymm. SO_2), 1312 s, 1150 v.s (symm. SO_2), 768 m, 748 m, 702 m, 525 m. ^{1}H NMR spectrum, δ, ppm: 3.16 d (1H, CH_2, *J* 15.6 Hz), 3.30 d (1H, CH_2, *J* 15.6 Hz), 3.52 s (3H, CH_3). ^{13}C NMR spectrum, δ, ppm: 36.8 (CH_3), 39.1 (C^4), 104.0 (C^5), 104.2 (C^3), 126.7 ($2C_{arom}$), 126.8 ($2C_{arom}$), 128.2 ($1C_{arom}$), 128.4 ($1C_{arom}$), 128.83 ($2C_{arom}$), 128.85 ($2C_{arom}$), 139.4 w ($1C_{arom}$), 141.9 w ($1C_{arom}$). Found, %: C 50.58; H 3.92; N 7.31; S 8.50. $C_{16}H_{15}N_2O_2S$. Calculated, %: C 50.67; H 3.99; N 7.39; S 8.45.

3-Bromo-5,5-diphenyl-3-(phenylsulfonyl)-Δ^1-pyrazoline (13). Yield 56%, mp 117–118°C (decomp.). IR spectrum, ν, cm^{-1}: 1451 m, 1327 s (asymm. SO_2), 1312 m, 1154 v.s (symm. SO_2), 760 m, 745 m, 706 m, 691 m, 590 m, 563 m, 540 s. ^{1}H NMR spectrum, δ, ppm: 3.27 d (1H, CH_2, *J* 15.6 Hz), 3.39 d (1H, CH_2, *J* 15.6 Hz), 7.19 d ($2H_{arom}$, *J* 9.6 Hz), 7.27–7.37 m ($8H_{arom}$), 7.61 t ($2H_{arom}$, *J* 7.5 Hz), 7.74 t ($1H_{arom}$, *J* 6.3 Hz), 8.13 d ($2H_{arom}$, *J* 8.5 Hz). ^{13}C NMR spectrum, δ, ppm: 41.2 (CH_2), 103.5 and 105.9 (C^3 and C^5), 126.8, 126.9, 128.3, 128.4, 128.9, 129.0, 129.1, 131.8, 133.3, 135.3, 139.7, 142.3. Found, %: C 57.19; H 3.90; N 6.28; S 7.16. $C_{21}H_{17}BrN_2O_2S$. Calculated, %: C 57.15; H 3.88; N 6.35; S 7.26.

1-Bromo-2,2-diphenyl-1-(methylsulfonyl)-cyclopropane (14). Yield 89%. Colorless crystals, mp 168°C (decomp.). IR spectrum, ν, cm^{-1}: 1312 v.s (asymm. SO_2), 1154 s (symm. SO_2). 795 m, 532 m, 494 m. ^{1}H NMR spectrum, δ, ppm: 2.24 d (1H, CH_2, *J* 6.9 Hz), 2.89 d (1H, CH_2, *J* 6.9 Hz), 3.18 s (3H, CH_3), 7.23–7.41 m ($6H_{arom}$), 7.55 d ($2H_{arom}$, *J* 8.3 Hz), 7.57 d ($2H_{arom}$, *J* 8.3 Hz). ^{13}C NMR spectrum, δ, ppm: 27.2 (CH_2), 40.4 (CH_3), 46.5 (C^2), 53.2 (C^1), 127.5 ($1C_{arom}$), 127.6 ($1C_{arom}$), 128.3 ($2C_{arom}$), 128.52 ($2C_{arom}$), 128.55 ($2C_{arom}$), 128.9 ($2C_{arom}$), 138.3 w ($1C_{arom}$), 141.9 w ($1C_{arom}$). Found, %: C 54.78; H 4.42; S 9.15. $C_{16}H_{15}BrO_2S$. Calculated, %: C 54.86; H 4.32; S 9.13.

1-Bromo-2,2-diphenyl-1-(phenylsulfonyl)cyclopropane (15). Yield 59%. Colorless crystals, mp 223–224°C (CH_2Cl_2–petroleum ether). IR spectrum, ν, cm^{-1}: 1446 s, 1311 v.s (asymm. SO_2), 1157 s (symm. SO_2), 1146 s, 1080 m, 787 s, 741 m, 702 s. 690 s, 579 s, 540 m. ^{1}H NMR spectrum, δ, ppm: 2.21 d (1H, CH_2, *J* 6.8 Hz), 3.04 d (1H, CH_2, *J* 6.8 Hz), 7.20–7.26 m ($2H_{arom}$), 7.29–7.35 m ($4H_{arom}$), 7.47–7.49 m ($2H_{arom}$), 7.53–7.57 m ($2H_{arom}$), 7.63–7.68 m ($2H_{arom}$), 7.90–7.93 m ($2H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 28.7 (CH_2), 47.0 (C^2), 54.6 (C^1), 127.63, 127.66, 128.6, 128.9, 129.0, 129.1, 129.9, 134.0, 138.79, 138.84, 142.5. Mass spectrum, *m/z* (I_{rel}, %): 412 (0.1) $[M]^{+\bullet}$, 269 (23), 270 (23), 271 (26), 272 (20), 191 (100) [M – SO_2Ph – Br], 189 (27), 190 (67), 192 (28), 165 (20), 115 (10), 77 (21), 51 (18). Found, %: C 60.97; H 4.22; S 7.85. $C_{21}H_{17}BrO_2S$. Calculated, %: C 61.02; H 4.15; S 7.76. M_{calc} 413.33.

X-ray diffraction analysis of cyclopropane (15). For the XRD experiment a transparent prism-like single crystal was selected of the size 0.32 × 0.14 × 0.12 mm. The array of diffraction reflections (overall 9884 reflections) was obtained on automatic four-circle diffractometer Oxford Diffraction Xcalibur Gemini S at 293(2) K (graphite monochromator, CCD detector Sapphire III, MoK_α-radiation, λ 0.71073 Å, ω-scanning, θ_{max} 30.51°, indices range $-8 \le h \le 8$, $-19 \le k \le 19$, $-31 \le l \le 31$). After averaging the equivalent reflections we obtained 5641 (R_{int} 0.0521) independent reflections, 4690 reflections with $I > 2\sigma(I)$. The processing of the diffraction reflections and the estimation of the unit cell parameters of the crystal was carried out applying CrysAlisPro program (Agilent Technologies, 2012) [40]. The primary fragment of the atomic structure of compound **15** was found by the direct method using SHELX-97 [41] and WinGX [42] software; the remaining nonhydrogen atoms were determined from the analysis of the difference synthesis of the electron density. The positions of hydrogen atoms in the structure of compound **15** were calculated geometrically and refined in the *rider* model [U(H) = 1.2U_{eq}(C)]. The positions of hydrogen atoms were found from the difference synthesis of the electron density and were refined in the general refining cycle without limitations. The extinction was accounted for empirically using the algorithm SCALE3 ABSPACK [40]. Crystals of compound **15** monoclinic, *a* 6.17670 (10), *b* 13.4687(2), *c* 22.3646(4) Å, β 94.896(2)°, *V* 1853.77(5) Å^3, *M* 236.18, *Z* 4, d_{calc} 1.481 g/cm^3, μ 2.341 mm^{-1}, *F*(000) 840, space group *P* 1 21/c 1. The number of independent refined parameters 234, *GOOF* 1.077. the scatter of the residual electron density –0.681 and 1.012 e·Å^{-3}. The final divergense factors:

R_1 0.0521 [for $I > 2\sigma(I)$], wR_2 0.0889 (for all independent reflections). Weighing scheme $w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 1.0621P]$, where $P = (F_o^2 + 2F_c^2)/3$. The data of the XRD study of compound **15** are deposited in the Cambridge Crystallographic Data Center (CCDC no. 1028707).

Reaction of Δ[1]-pyrazoline (12) with DBU. To a solution of 0.5 g (1.3 mmol) of compound **12** in 20 mL of anhydrous CH_2Cl_2 was added dropwise while stirring at 0°C 0.221 g (1.45 mmol) of DBU in 5 mL of the same solvent. The mixture was stirred at 20°C for 6 h, then it was filtered through a bed of silica gel (1 cm). On removing the solvent in a vacuum of the water-jet pump we obtained a mixture of compounds **16** and **17** in a ratio 0.6 : 1 (according to ^{1}H NMR data). The mixture was separated by flash-chromatography on silica gel.

5-Methylene-3,3-diphenyl-Δ[1]-pyrazoline (16). Yield 12%, mp 86°C. IR spectrum, ν, cm^{-1}: 1493 s, 1447 s, 903 m, 768 s, 752 s, 698 v.s, 637 s. ^{1}H NMR spectrum, δ, ppm: 3.02 t (2H, H^4, *J* 2.3 Hz), 5.67 m ($1H_{olefin}$), 6.19 m ($1H_{olefin}$), 7.25–7.36 m ($10H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 36.7 (C^4), 97.7 (C^3), 112.5 (olefin CH_2), 127.0 ($4C_{arom}$), 127.7 ($2C_{arom}$), 128.7 ($4C_{arom}$), 143.2 w ($2C_{arom}$), 168.6 (C^5). Found, %: C 82.17; H 6.11; N 11.85. $C_{16}H_{14}N_2$. Calculated, %: C 82.02; H 6.02; N 11.96.

5,5-Diphenyl-3-(methylsulfonyl)-Δ[2]-pyrazoline (17). Yield 36%, mp 112°C. IR spectrum, ν, cm^{-1}: 3310 m, 1447 m, 1316 m (asymm. SO_2), 1173 m (symm. SO_2), 1297 v.s, 1172 m, 1142 m, 1127 s, 764 s, 702 s, 567 m, 525 m. ^{1}H NMR spectrum, δ, ppm: 3.15 s (3H, CH_3), 3.71 s (2H, CH_2), 6.03 br.s (1H, NH), 7.23–7.40 m ($10H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 41.1 (C^4), 43.1 (CH_3), 77.1 (C^5), 126.4 ($4C_{arom}$), 128.1 ($2C_{arom}$), 129.0 ($4C_{arom}$), 144.2 w ($2C_{arom}$), 149.7 (C^3). Found, %: C 63.97; H 5.32; N 9.26; S 10.65. $C_{16}H_{16}N_2O_2S$. Calculated, %: C 63.98; H 5.37; N 9.33; S 10.67.

Reaction of vinyl methyl sulfone (18) with diphenyldiazomethane. The reaction was carried out in anhydrous ethyl ether at 20°C for 25 h similarly to reactions of vinyl sulfones **1a–1c**, **2b**, and **2c**. Δ[2]-Pyrazoline **17** was obtained in 81% yield and was identical to the product of hydrodebromination–isomerization of Δ[1]-pyrazoline **12**.

1-Methylsulfonyl-2,2-diphenylcyclopropane (19). The thermolysis of compound **17** was performed in the conditions of the experiment with Δ[2]-pyrazoline **5a**. Yield 55%, colorless crystals, mp 97–98°C. IR spectrum, ν, cm^{-1}: 3055 w, 3005 w, 1497 m, 146 m, 1323 m, 1296 v.s, 1138 v.s, 945 m, 779 m, 752 m, 706 s, 698 m, 528 m. ^{1}H NMR spectrum, δ, ppm: 1.82 d.d (1H, H^3, *J* 5.6, 8.8 Hz), 2.48 t (1H, H^3, *J* 5.6 Hz), 3.86 s (3H, CH_3), 3.24 d.d (1H, H^1, *J* 5.6, 8.8 Hz), 7.22–7.36 m ($8H_{arom}$), 7.48–7.51 m ($2H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 18.0 (C^3), 40.0 (C^2), 42.4 (CH_3), 43.9 (C^1), 127.4 ($1C_{arom}$), 127.7 ($1C_{arom}$), 128.1 ($2C_{arom}$), 128.5 ($2C_{arom}$), 128.9 ($2C_{arom}$), 137.1 w ($1C_{arom}$), 143.6 w ($1C_{arom}$). Found, %: C 70.67; H 5.82; S 11.65. $C_{16}H_{16}O_2S$. Calculated, %: C 70.56; H 5.92; S 11.77.

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