FULL PAPER

Reactions of Diazomethanes with 5-Benzylidene-3-phenylrhodanine – A Computational Study

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Dedicated to Professor *Grzegorz Mlostoń*, University of Łódź, on the occasion of his 65th birthday

It has been shown previously that the reaction of diazomethane with 5-benzylidene-3-phenylrhodanine (**1**) in THF at −20° occurs at the exocyclic C=C bond *via* cyclopropanation to give **3a** and methylation to yield **4**, respectively, whereas the corresponding reaction with phenyldiazomethane in toluene at 0° leads to the cyclopropane derivative **3b** exclusively. Surprisingly, under similar conditions, no reaction was observed between **1** and diphenyldiazomethane, but the 2-diphenylmethylidene derivative **5** was formed in boiling toluene. In the present study, these results have been rationalized by calculations at the DFT B3LYP/6-31G(d) level using PCM solvent model. In the case of diazomethane, the formation of **3a** occurs *via* initial *Michael* addition, whereas **4** is formed *via* [3+2] cycloaddition followed by N_2 elimination and H-migration. The preferred pathway of the reaction of **1** with phenyldiazomethane is a [3+2] cycloaddition, subsequent N_2 elimination and ring closure of an intermediate zwitterion to give **3b**. Finally, the calculations show that the energetically most favorable reaction of **1** with diphenyldiazomethane is the initial formation of diphenylcarbene, which adds to the S-atom to give a thiocarbonyl ylide, followed by 1,3-dipolar electrocyclization and S-elimination.

Introduction. – Within the syntheses of five-membered heterocycles, 1,3-dipolar cycloadditions are of great significance. The concept of this type of a pericyclic reaction [1] has been formulated by *Huisgen* [2], and a large series of review articles demonstrate their importance (*e.g.*, [3]). The specific features of these reactions, *i.e.*, their chemo-, regio-, and stereoselectivity, are nowadays well-understood and predictable on the basis of theoretical concepts such as the Frontier Molecular Orbital (FMO) theory [4].

The experimental results of 1,3-dipolar cycloadditions with C=C, C=O, and C=N groups as dipolarophiles are, in general, in accordance with the FMO predictions for [3+2] cycloadditions. However, some examples are known to proceed in a non-concerted manner *via* zwitterionic intermediates [5]. On the other hand, the reactions with C=S groups offered some surprise, *e.g.*, an extraordinary reactivity [6]. For that reason, thioketones were named 'superdipolarophiles'. Furthermore, it has been shown that some of the formal 1,3-dipolar cycloadditions with C=S dipolarophiles occur *via* a two-step mechanism with an intermediate biradical [7].

Whereas the preferred C=S dipolarophiles are aromatic and cycloaliphatic thioketones, heterocyclic thiones, *e.g.*, 4,4-disubstituted 1,3-thiazole-5(4*H*)-thiones [8][9] and 5-benzylidene-3-phenylrhodanine (**1**) [10], have also been used in 1,3-dipolar cycloadditions. In these studies, the chemo(site)selectivity was the main issue, as in the first case, a C=N group was present besides the C=S group, whereas in the case of **1**, the C=C, C=O, and C=S groups could act as dipolarophiles. Recently, amino-catalyzed asymmetric *Diels–Alder* reactions of **1** with 2,4-dienals or 4-phenylbut-3-en-2-ones were reported to occur exclusively at the exocyclic C=C bond [11]. On the other hand, 1,3-dipolar cycloadditions of benzonitrile imines and **1** yielded spiroheterocyclic compounds *via* addition to the C=S group [10a–10d], whereas with cycloaliphatic thiocarbonyl-ylides additions to the C=C bond were observed [10e]. In the case of thiobenzophenone *S*-methanide, a competitive addition onto the C=C and C=S groups took place with preference of the C=C bond.

Some time ago, we reported on the reactions of diazomethane (**2a**), phenyldiazomethane (**2b**), and diphenyldiazomethane (**2c**) with **1** [10f]. Whereas with **2a** and **2b**, only products of the C=C addition, *i.e.*, cyclopropane derivatives **3** and, in the case of **2a**, the methylated product **4**, were obtained, the reaction of **2c** occurred exclusively at the C=S group to give **5** (*Scheme 1*). The formation of products **3** and **4** may be explained by a [3+2] cycloaddition of **2a** and **2b**, respectively, onto the C=C bond of **1**, in analogy to the reactions with cycloaliphatic thiocarbonyl ylides [10e], followed by the extrusion of N_2 and cyclization or H-shift. But a stepwise mechanism initiated by a *Michael* addition of the diazo compound onto the benzylidene group may also lead to the observed products. On the other hand, [3+2] cycloaddition of **2c** with the C=S group of **1** as in the reactions with benzonitrile imines

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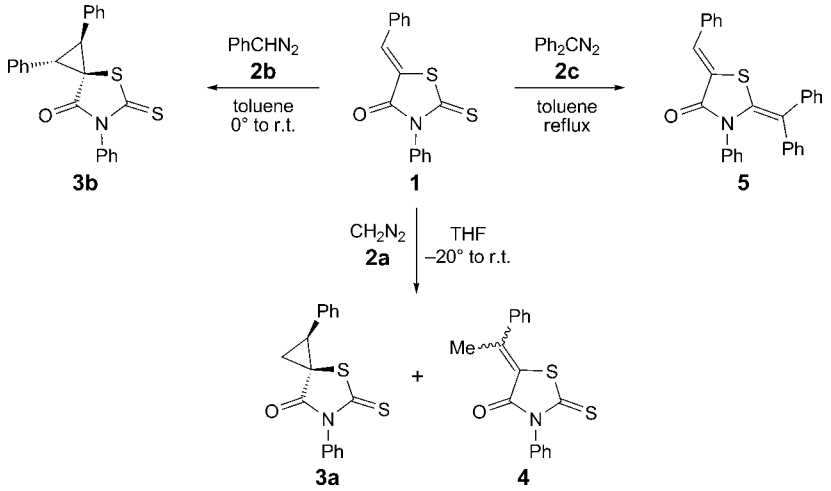
Scheme 1



[10a – 10d] and subsequent 'two-fold extrusion' of N_2 and S [12] would lead to product **5**.

The goal of the present study was to rationalize the results shown in *Scheme 1* on the basis of quantum-chemical calculations.

Results and Discussion. – In general, the reactivity of 1,3-dipolar cycloadditions can be understood on the basis of the FMO theory: the smaller the gap between the $HOMO_{(Dipole)}/LUMO_{(Dipolarophile)}$ and $LUMO_{(Dipole)}/HOMO_{(Dipolarophile)}$, respectively, the stronger is the stabilization of the transition state as a result of the HOMO/LUMO interaction, and the higher is the reactivity. If the reaction partner of a 1,3-dipole contains more than one dipolarophilic π-system, the chemoselectivity of the reaction can be explained analogously. According to *Sustmann*'s classification, diazoalkanes belong to the type I dipoles with relatively high lying HOMO and LUMO [4f]. Therefore, their 1,3-dipolar cycloadditions with typical C=C dipolarophiles are $HOMO_{(Dipole)}/LUMO_{(Dipolarophile)}$-controlled reactions [4g]. Because of the low-lying LUMO of the C=S group of thioketones [4h], the reactions of diazoalkanes with thioketones are fast [6a]. With the same argument, the chemoselective C=S addition in the reactions of **1** with nitrile imines (type II dipoles [4f]) was rationalized [10a – 10d].

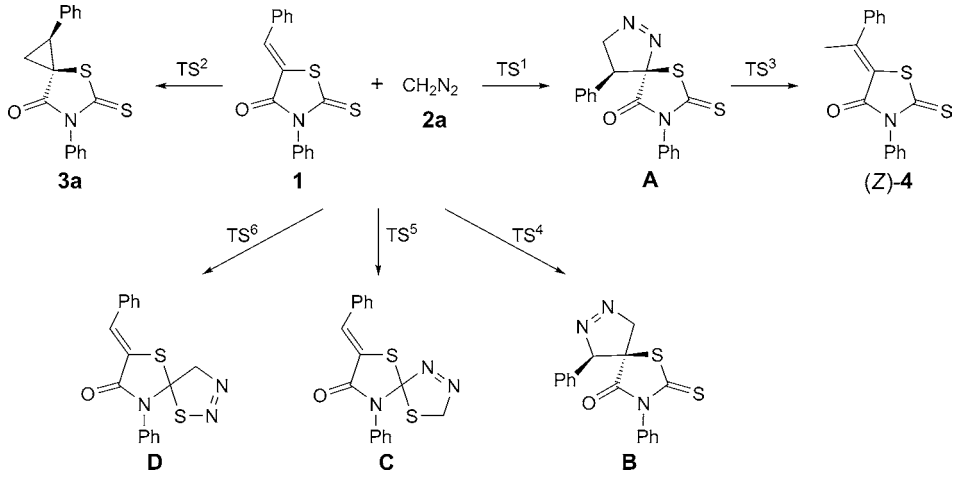
In our study on the 1,3-dipolar cycloaddition of **2a – 2c** with **1**, all reactions occurred smoothly in THF at $-20°$ to room temperature, in toluene at 0° to room temperature, and in boiling toluene, respectively, leading to the products in high yields [10f] (*Scheme 1*). But on the basis of the FMO theory, the observed difference in the chemoselectivity of the reactions cannot be explained. The LUMO of **1** (−2.65 eV in THF and −2.59 eV in toluene, resp., calculated at the DFT B3LYP/6 – 31G(d) level with PCM solvent model) shows the correct orbital symmetry of the C=S, C=O, and C=C fragments for the 1,3-dipolar cycloaddition with diazoalkanes. The energy differences between the LUMO of **1** and the HOMOs of **2a** (−5.99 eV, in THF), **2b** (−5.42 eV, in toluene), and **2c** (−5.24 eV, in toluene) are all significantly smaller than those between the HOMO of **1** (−6.23 and −6.19 eV, in THF and toluene, resp.) and the LUMOs of the diazoalkanes **2** (**2a**: −1.26 eV, in THF; **2b**: −1.52 eV, in toluene; **2c**: −1.54 eV, in toluene). Therefore, one could expect analogous reactions for all three diazo compounds **2a – 2c**.

As FMO considerations do not allow explaining the different pathways of the reactions of **1** with **2a – 2c**, the free energy profiles of the various transformations were computed at the DFT B3LYP/6-31G(d) level with PCM solvent model.

According to the calculations of the reaction of **1** with CH_2N_2 (**2a**) in THF, the main product should be (*Z*)-**4** (*Scheme 2*, *Fig. 1*), which was indeed obtained as the major product in a *ca.* 3 : 1 mixture of (*Z*)- and (*E*)-isomer [10f]. Its formation proceeds *via* the [3 + 2] cycloaddition to give pyrazoline **A** (TS^1, 27.3 kcal mol^{-1}). Decomposition of the latter leads directly to product (*Z*)-**4** *via* simultaneous elimination of N_2 and H-migration (TS^3, 24.0 kcal mol^{-1}). On the other hand, the formation of cyclopropane derivative **3a** occurs *via* the *Michael* type attack of CH_2 of **2a** at C(γ) of the C=C–C=O system (TS^2, 28.5 kcal mol^{-1}). According to these results, the products **4** and **3a** should be formed in a ratio of 78 : 22, which is in reasonable agreement with the found ratio (*ca.* 65 : 35). Furthermore, neither the [3 + 2] cycloaddition of **1** and **2a** to give the regioisomeric pyrazoline **B** (TS^4, 34.8 kcal mol^{-1}) nor those involving the C=S bond leading to thiadazolines **C** and **D** (TS^5, 32.1 kcal mol^{-1} and TS^6, 33.9 kcal mol^{-1}, resp.) can compete with the formation of **A** because of much higher energies of the corresponding transition states. Furthermore, the formations of the 1,3,4-thiadiazole derivatives **C** and **D** are endothermic reactions and, therefore, these products cannot be observed directly in this reaction.

In summary, the reaction of **2a** with **1** occurs chemo-, regio-, and stereoselectively at the exocyclic C=C bond to give (*Z*)-**4** and **3a** and not at the C=S bond. But it is worth mentioning that only (*Z*)-**4** is formed *via* initial [3 + 2] cycloaddition, whereas an initial *Michael* addition is responsible for the formation of **3a**. The formation of

Scheme 2



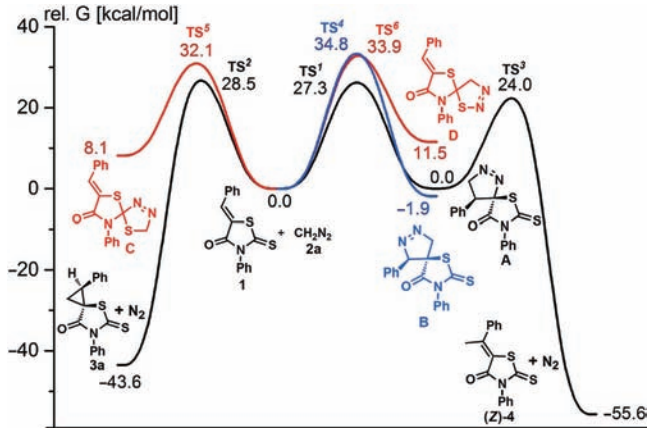


Fig. 1. *Energy profiles for the reaction of* **1** *and* CH_2N_2 (**2a**) *in THF.* Relative free *Gibbs* energies (in kcal mol^{-1}, 298 K, PCM model for THF) computed at the DFT B3LYP/6 – 31G(d) level.

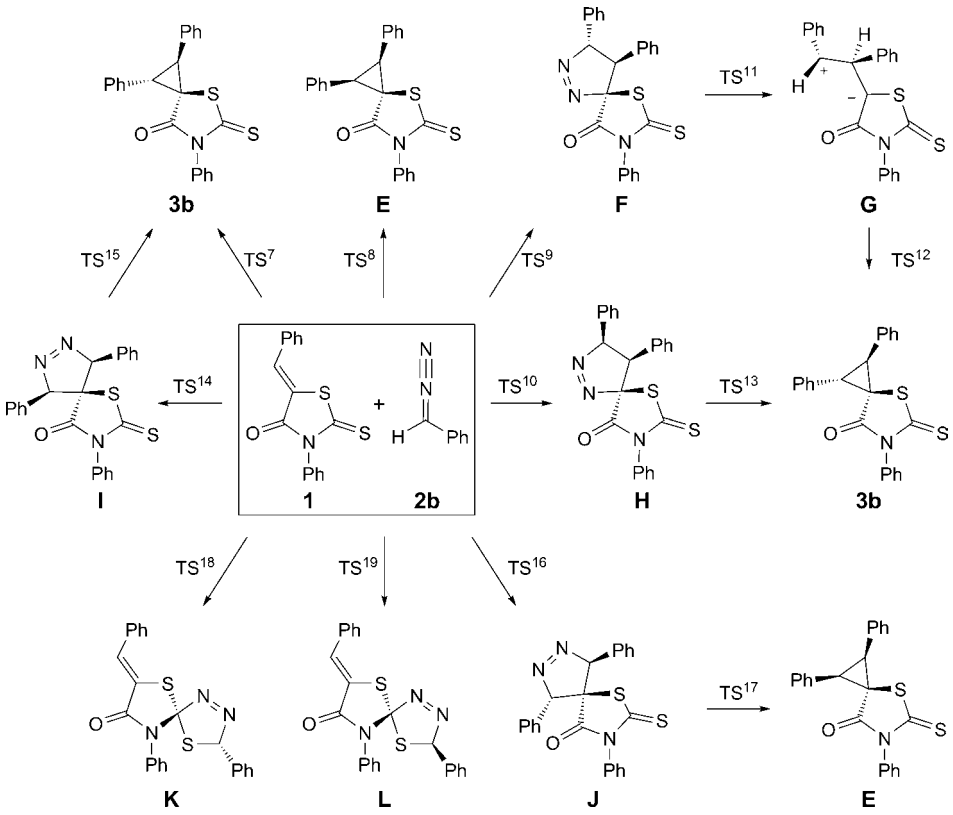
carbene (:CH_2) from CH_2N_2 under the reaction conditions is impossible and, therefore, this reaction pathway was not taken into account. It has to be mentioned that the entropy contribution to the activation barrier can be overvalued in the framework of the model used thereby giving inflated free energies of the transition states. For this reason, the corresponding figure in terms of enthalpy is deposited in an electronic supporting information (ESI).

In analogy to the reaction of **1** and **2a** (*Scheme 2*), various reaction courses for that of **1** and **2b** in toluene were calculated (*Scheme 3*). The computation of the *Michael*-type pathway for the formation of **3b** or its *cis*-isomer **E** in analogy to **1** + **2a** → **3a** (*Scheme 2*) indicate significant higher energies for the corresponding transition states TS^7 (39.3 kcal mol^{-1}) and TS^8 (38.4 kcal mol^{-1}), respectively (*Fig. 2*). From the data of *Fig. 2*, it can be seen that the least energy route to **3b** is **1** + **2b** → [TS^9] → **F** → [TS^{11}] → **G** → [TS^{12}] → **3b** with TS^9 (31.2 kcal mol^{-1}) as the highest energy barrier, and consequently, the *trans*-configured spirocyclopropane derivative **3b** has to be the main product of the reaction, in accordance with the experiment. That means that the formation of **3b** proceeds *via* [3 + 2] cycloaddition at the exocyclic C=C bond to give the *trans*-spirodihydro-1,2-diazole **F**, followed by N_2 elimination leading to the zwitterion **G**, and subsequent ring closure to yield the sterically less congested *trans*-substituted derivative **3b**. The alternative [3 + 2] cycloaddition leading to the diastereoisomeric *cis*-spirodihydro-1,2-diazole **H** is less favored (TS^{10} = 33.6 kcal mol^{-1}). Nevertheless, the second low-energy route to **3b** is **1** + **2b** → [TS^{10}] → **H** → [TS^{13}] → **3b**, and the ratio of product **3b** formed *via* these two pathways should be *ca.* 98 : 2. The [3 + 2] cycloadditions resulting in the regioisomeric spirodihydro-1,2-diazoles **I** and **J** (TS^{14} = 36.5 kcal mol^{-1} and TS^{16} = 36.8 kcal mol^{-1}, resp.) are even less favored and cannot compete with the formation of **F** and **H**. Furthermore, the activation energies for the transformations **I** → [TS^{15}] → **3b** and **J** → [TS^{17}] → **E** (42.2 and 44.1 kcal mol^{-1}, resp.) are prohibitive. Finally, similar to the reaction of **1** with CH_2N_2 (**2a**, *Scheme 2*), the formation of spiro-1,3,4-thiadiazolines **K** and **L** are endothermic processes, and the transition state energies of the corresponding [3 + 2] cycloaddition of **2b** onto the C=S group of **1** are 34.3 (TS^{18}) and 34.5 kcal mol^{-1} (TS^{19}), respectively.

In summary, the calculations rationalized the selective formation of **3b** in the reaction of **1** with **2b** *via* [3 + 2] cycloaddition at the exocyclic C=C bond of **1** as the most dipolarophilic structure moiety. The reaction route *via* formation of phenylcarbene (:CHPh) in this case was not considered, because the barrier of its formation from $PhCHN_2$ (34.5 kcal mol^{-1}) is much higher than the barrier for the transformation **1** + **2b** → [TS^9] → **F** (31.2 kcal mol^{-1}).

In contrast to the reactions of **1** with **2a** and **2b**, the calculations for the reaction with **2c** in toluene show that the activation energy for the [3 + 2] cycloaddition with the C=S group leading to the spiro-1,3,4-thiadiazoline **M** (TS^{20} = 38.2 kcal mol^{-1}) is lower than that for the [3 + 2] cycloaddition with the C=C moiety leading to the spiro-1,2-diazolidine **N** (TS^{21} = 40.9 kcal mol^{-1}; *Scheme 4*, *Fig. 3*). Therefore, the formation of the observed product **5** could

Scheme 3



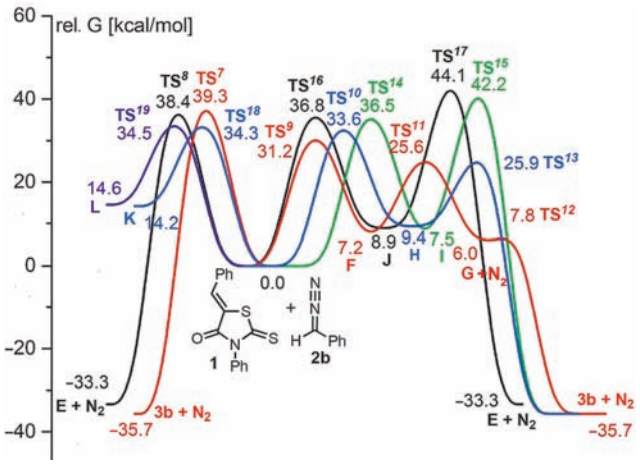
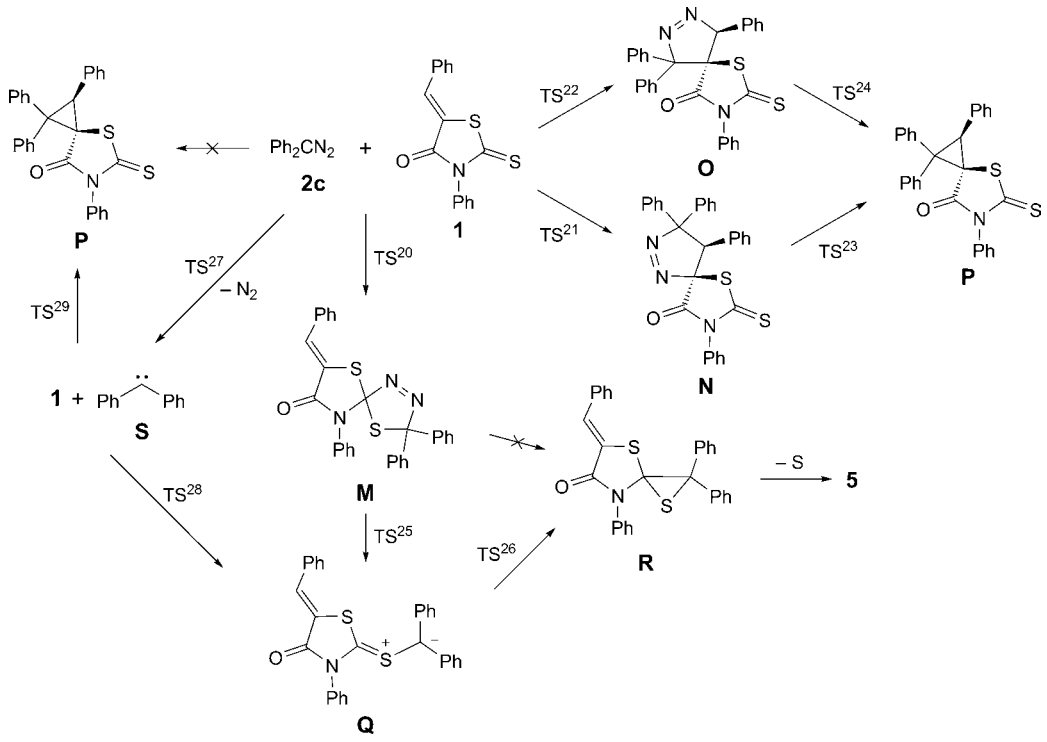


Fig. 2. *Energy profiles for the reaction of* **1** *and* $PhCHN_2$ (**2b**) *in toluene*. Relative free *Gibbs* energies (in kcal mol^{-1}, 298 K, PCM model for toluene) computed at the DFT B3LYP/6-31G(d) level.

be rationalized by the reaction course **1** + **2c** → [TS^{20}] → **M** → [TS^{25}] → **Q** → [TS^{26}] → **R** → **5**, *i.e.*, the initially formed **M** eliminates N_2 to give the zwitterion **Q** (TS^{25} = 33.7 kcal mol^{-1}), which subsequently forms the thiirane **R** *via* 1,3-dipolar electrocyclization (TS^{26} = 6.9 kcal mol^{-1}). Finally, extrusion of sulfur yields **5**. But the results presented in *Fig. 3* show that the transformation of diphenyldiazomethane (**2c**) to diphenylcarbene (**S**) proceeds *via* a lower energy barrier (TS^{27} = 30.9 kcal mol^{-1}) than any cycloaddition of **2c** to the C=C or C=S groups of **1**. Then, carbene **S** reacts smoothly with the C=S group of **1** to give the thiocarbonyl ylide **Q** (TS^{28} = 24.2 kcal mol^{-1}). The cycloaddition of **S** to the C=C group of **1** with formation of spirocyclopropane **P** (TS^{29} = 32.9 kcal mol^{-1}) cannot compete with the attack at the C=S group, which leads to **Q**.

Conclusions. – The computations of various courses of the reactions of **1** with the diazo compounds **2a** – **2c** rationalize the surprising results obtained in the experiments [10f]. They show that different reaction pathways are responsible. In the reaction with **2a**, the formations of **4** and **3a** *via* initial [3 + 2] cycloaddition and *Michael*-type addition, respectively, are the favored processes. The alternative [3 + 2] cycloadditions with the C=S group cannot compete. Similarly, in the case of **2b**, the reaction with the lowest activation energy is the [3 + 2] cycloaddition with the C=C group to form the dihydro-1,2-pyrazole **F** as an intermediate, which then reacts in a two-step process to give the observed product **3b**. Again, the [3 + 2] cycloadditions with the C=S group are not competitive because their transition state energies are significantly higher. Finally, in the case of diphenyldiazomethane (**2c**), the activation energies for the [3 + 2] cycloadditions with the C=C as well as with the C=S group are rather high and, therefore, no reaction takes place at room temperature [10f]. The lowest transition state energy was calculated for the generation of diphenylcarbene (**S**) from **2c**,

Scheme 4



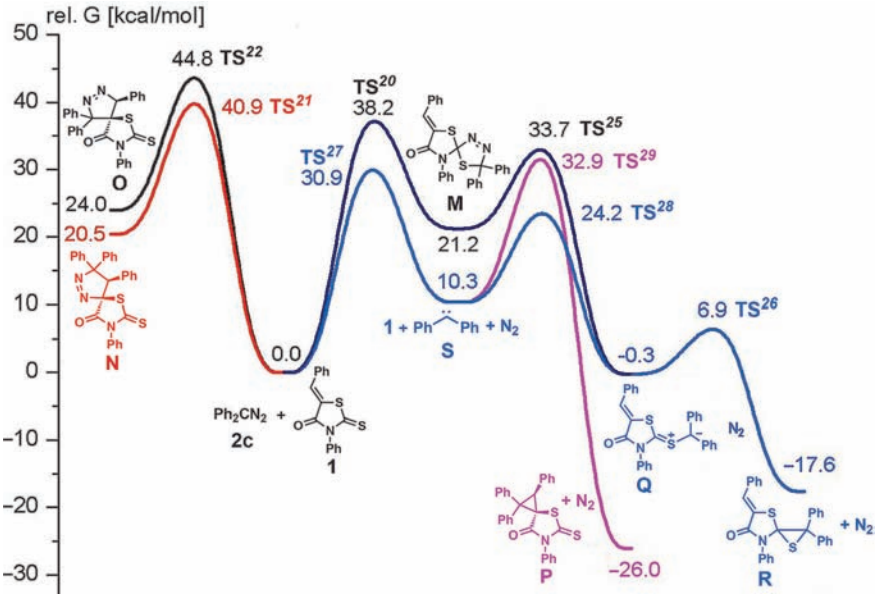


Fig. 3. *Energy profiles for the reaction of* **1** *and* Ph_2CN_2 (**2c**) *in toluene.* Relative free *Gibbs* energies (in kcal mol^{-1}, 298 K, PCM model for toluene) computed at the DFT B3LYP/6 – 31G(d) level.

which then adds to the C=S group in a known manner forming an intermediate thiocarbonyl ylide **Q**. The latter then cyclizes to give thiirane **R**, and the elimination of the S-atom leads to the observed product **5** [13].

Calculations. All calculations were carried out at the DFT B3LYP/6-31G(d) level [14] by using the Gaussian 09 suite of quantum-chemical programs [15]. Geometry optimizations of intermediates, transition states, reactants, and products in THF or toluene were performed using PCM model. Intrinsic reaction coordinates were calculated to authenticate all transition states.

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