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Azulenylcarbene and Naphthylcarbene Isomerizations. Falling Solid Flash Vacuum Pyrolysis

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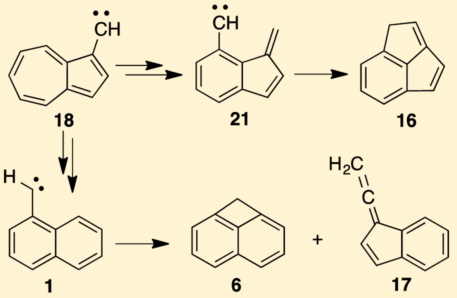
Supporting Information

ABSTRACT: 1-Azulenylcarbene **18** has been generated from 5-(1-azulenyl)-tetrazole and the sodium salt of azulene-1-carbaldehyde tosylhydrazone using the falling solid flash vacuum pyrolysis (FS-FVP) method. The principal products, which are also formed from both 1- and 2-naphthylcarbenes, cyclobuta[*de*]-naphthalene **6**, cyclopenta[*cd*]indene **16**, and benzofulvenallene **17**, are explained in terms of two reaction paths, (a) a rearrangement to benzofulvenyl-7-carbene **13** and (b) a rearrangement to 1-naphthylcarbene **1**. Moreover, **16** is also formed from 2-azulenylcarbene **30**, thereby indicating the occurrence of a 2-azulenylcarbene−1-azulenylcarbene rearrangement. The reaction mechanisms are supported by density functional theory calculations at the B3LYP/6-31G** level, which indicate that all the rearrangements have activation barriers of <35 kcal/mol, thus making them readily achievable under FVP conditions.



INTRODUCTION

The rich rearrangement chemistry of the naphthylcarbenes has been the subject of detailed investigation under both thermal and photochemical reaction conditions.[1] The thermal interconversion of 1- and 2-naphthylcarbenes **1** and **5**, and the rearrangement of both of them to cyclobuta[*de*]naphthalene **6** as the global energy minimum, were established in 1980 and summarized in Scheme 1.[2−4]

The energy profile has been evaluated at the B3LYP/6-311+G*//B3LYP/6-31G* level, which indicated that tricyclic cyclopropenes **2** and **4** are transition states.[5] However, the carbenes can also form two other tricyclic cyclopropenes, **7** and **10**, which represent energy minima (Scheme 2).[3,5] Cyclopropenes **7** and **10** were identified in Ar matrices under photochemical conditions.[6] The carbenes, tricyclic cyclopropenes, benzocycloheptatetraenes, and corresponding benzocycloheptatrienylidenes have been the subject of further, extensive investigation.[7,8]

Notably, in spite of their nonaromatic character and consequential high energies, rearrangements through transition structures **2TS** and **4TS** are efficient under flash vacuum pyrolysis (FVP) conditions.[2,3] Our calculations of Gibbs free energies at the B3LYP/6-31G** level afford an overall barrier for the interconversion of **1** and **5** at 600 °C of ∼30 kcal/mol, and it is only ∼16 kcal/mol for the cyclization of **1** to **6** on the singlet energy surface (see Scheme 3).

Moreover, rearrangement to the tricyclic cyclobuta[*cd*]-indene **16** and benzofulvenallene **17** also takes place to a minor extent in the FVP reactions of both 1- and 2-naphthylcarbenes.[3] These reactions can be formulated as indicated in Scheme 3 on the basis of analogy with the ring contraction of phenylcarbene to fulvenallene.[9] The lowest-energy paths to these products have activation barriers of no more than 35 kcal/mol (Scheme 3). Benzofulvenylcarbene **13** has been generated independently by FVP of diazo compound **14**, which yielded **15** at the lowest temperatures, and **16** and **17** at higher temperatures.[9,10]

In contrast to these extensive studies, little is known about the isomeric azulenylcarbenes. However, Sander and coworkers recently published an intriguing reaction, the tunneling 1,4-H (or 1,10-H) shift converting 1-azulenylcarbene **18** to fulvene derivative **19** under matrix isolation condition (Scheme 4).[11] The calculated classical barrier for the 1,9-H shift at the RCCSD(T)/cc-pVTZ//(U)B3LYP/cc-pVTZ level was only ∼23 kcal/mol.[11] Although this is far too high for the classical process in the Ar or Ne matrix at 3−10 K, it will be very facile under FVP conditions. This observation prompts us to report our investigation of the pyrolytic behavior of 1- and 2-azulenylcarbenes.

RESULTS AND DISCUSSION

1-Azulenylcarbene **18** was generated from two different precursors, the 1-azulenecarbaldehyde tosylhydrazone sodium salt and 5-(1-azulenyl)tetrazole (Scheme 5). Both precursors are expected to generate 1-diazomethylazulene, and this was supported by the observation of an IR absorption at 2040 cm^{-1} in the 77 K IR spectrum of the products resulting from mild pyrolysis. However, both these precursors are too involatile for conventional FVP, with the consequence that only very limited amounts of products can be obtained in a reasonable time. Instead, we applied falling solid flash vacuum pyrolysis (FS-

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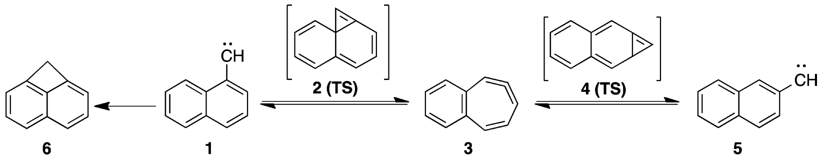
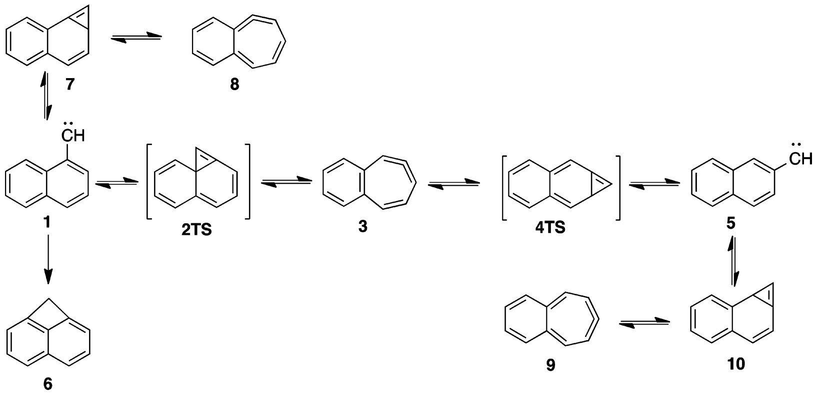
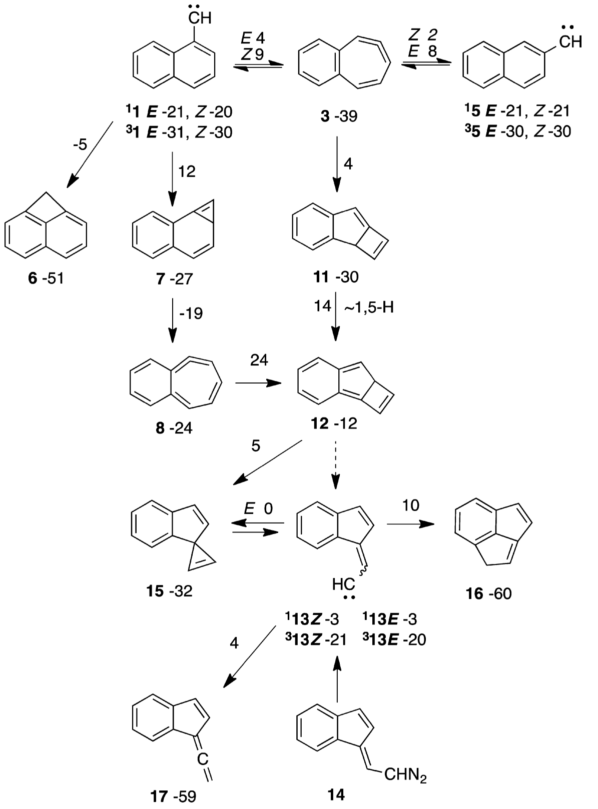
Scheme 1. 2-Naphthylcarbene−1-Naphthylcarbene−Cyclobuta[*de*]naphthalene Rearrangement



Scheme 2. Naphthylcarbene−Benzobicyclo[4.1.0]heptatriene−Benzocycloheptatetraene Rearrangements

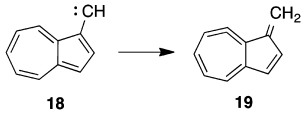


Scheme 3. Thermal Rearrangements of the Naphthylcarbenes^a

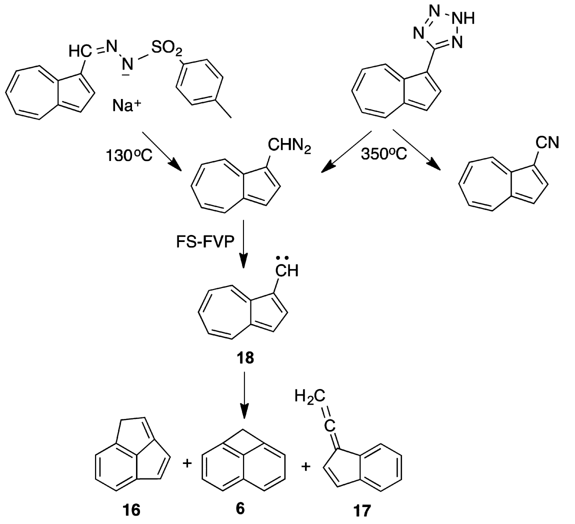


^{a}Numbers in normal font are Gibbs free energies (ΔG) in kilocalories per mole at 873 K calculated at the B3LYP/6-31G** level, relative to ^{1}**18**E = 0 (see Scheme 6). Relative energies of transition states are indicated above the arrows. See the Supporting Information for an analogous scheme with electronic energies E and computational details.

Scheme 4. Tunneling 1-Azulenylcarbene Rearrangement Reported by Sander et al.[11]



Scheme 5. Products (**6**, **16**, and **17**) of the Falling Solid Flash Vacuum Pyrolysis (FS-FVP) of Precursors of 1-Azulenylcarbene **18**



FVP).[12] Using this technique, the solid tosylhydrazone sodium salt was pyrolyzed at 600 °C and 5-(1-azulenyl)tetrazole at 800 °C. The products were isolated in liquid N_2 traps and examined by gas chromatography and NMR spectroscopy. Comparison with the samples characterized previously[3,4,10] permitted the identification of **6**, **16**, and **17**, i.e., the same products that were obtained from the naphthylcarbenes (formation of **15** would not be observable at these reaction temperatures, as it reverts to **13** and hence **16** and **17**). In addition, the pyrolysis of 5-substituted tetrazoles always results in some cycloreversion to HN_3 and a nitrile,[9] in this case azulene-1-carbonitrile.

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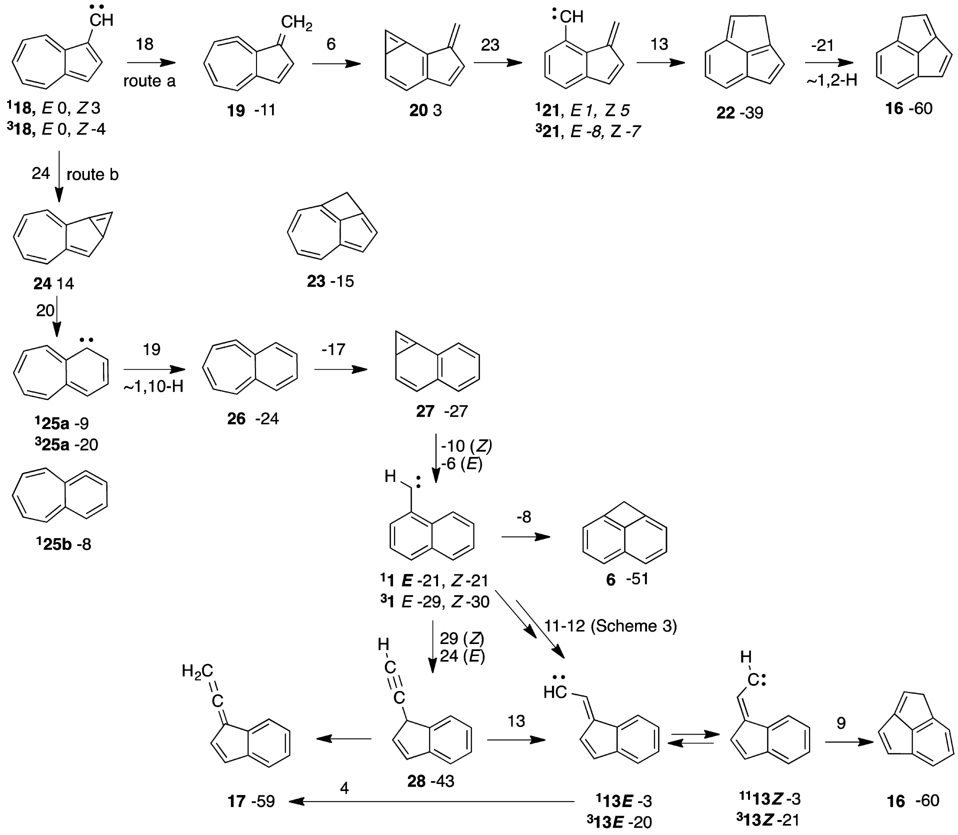
Scheme 6. Thermal Rearrangements of 1-Azulenylcarbene **18**[a]



[a] Numbers in normal font are Gibbs free energies (ΔG) in kilocalories per mole at 873 K calculated at the B3LYP/6-31G** level, relative to ^{1}**18**E = 0. Relative energies of transition states are indicated above the arrows. See the Supporting Information for an analogous scheme with electronic energies E and computational details.

The formation of **16** is readily explained in terms of the **18** → **19** Sander rearrangement and then **19** → **20** → **21** (path a, Scheme 6). The latter reaction, **19** → **20** → **21**, is simply a cycloheptatetraene−phenylcarbene rearrangement; the **21** → **22** reaction is an electrocyclization, and the **22** → **16** reaction is a 1,2-H shift. All these steps have very modest calculated activation barriers of no more than 23 kcal/mol, which will be very readily accessible under FVP conditions.

A cyclobuta[*cd*]azulene **23** was not isolated (see Scheme 6). This is understandable in terms of the calculated free energy at the B3LYP/6-31G** level, which is ~36 kcal/mol higher than that of cyclobuta[*de*]naphthalene **6** at 600 °C. Therefore, it could be that a potentially formed cyclobuta[*cd*]azulene **23** rearranges to **6** via an azulene−naphthalene rearrangement;[13] but this is a very high energy process with an activation barrier of the order of 70 kcal/mol, which requires a temperature of >1000 °C in our apparatus. It was desirable, therefore, to explore lower-energy pathways to **6**. Such a path has been found in the **18** → **24** → **25** → **26** → **27** transformations leading to 1-naphthylcarbene **1** (path b, Scheme 6). The triplet state of carbene **25a** was identified in the matrix photolysis study.[10] On the singlet energy surface, the corresponding six-membered cyclic allene **25b** is also a possibility, analogous to heterocyclic allenes investigated by Sheridan et al.[14] The singlet carbene ^{1}**25a** is very nearly planar, but a twisted allene-type structure **25b** with nearly the same energy also exists (see Scheme 6). A CASSCF calculation also yielded identical energies for ^{1}**25a** and **25b**, 3.3 kcal/mol above that of ^{3}**25a**.

From 1-naphthylcarbene **1**, familiar products **6** and **16** can now be formed. The cyclization to cyclobutanaphthalene **6** is very facile (Scheme 6), and the transition state was confirmed by an IRC calculation. There are in principle two routes from **1** to **16** and **17**: one by the paths shown in Scheme 3 with a maximal activation barrier of 35 kcal/mol, which is analogous to the phenylcarbene−fulvenallene rearrangement,[9] and the other via direct ring contraction of **1** to 1-ethynylindene **28** [barrier of ~50 kcal/mol (Scheme 6)]. Thus, the transannular cyclization path via **11** and/or **12** (Scheme 3) is clearly preferred. From **12** and **28**, there are low-energy paths to benzofulvenylcarbenes **13a** and **13b**, which then cyclizes easily to **16**. Thus, there are potentially two paths to **16**, via routes a and b (Scheme 6). As in the case for fulvenallene and 5-ethynylcyclopentadiene,[9] any interconversion between **28** and **17** is likely to be collision-induced rather than a unimolecular, pericyclic 1,3-H shift.

It is noteworthy that the ratio of cyclopenta[*cd*]indene **16** to cyclobuta[*de*]naphthalene **6** is much higher in the 600 °C pyrolysis of the tosylhydrazone salt than in the 800 °C pyrolysis of the tetrazole. Furthermore, benzofulvenallene **17** was only clearly identified in the high-temperature pyrolysis of the tetrazole. There may be several reasons for this outcome, but it might reflect the fact that the first step of route a has an activation barrier considerably lower than that of path b. Thus, formation of **16** will be preferred at lower temperatures. Formation of 1-naphthylcarbene and its rearrangement products will become more competitive at high temperatures.

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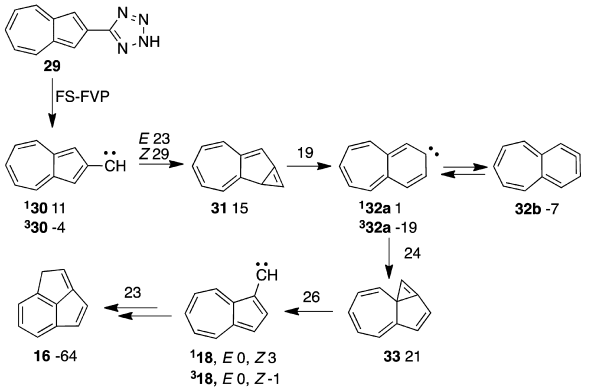
2-Azulenylcarbene **30** was examined in a similar manner by subjecting 2-(5-azulenyl)tetrazole to FS-FVP. The 2-azulenyldiazomethane could be detected by an IR absorption at 2060 cm^{-1} when using a pyrolysis temperature of 350 °C. At 600 °C, cycloreversion to azulene-2-carbonitrile and HN_3 was the major reaction channel, and consequently, the yield of $C_{11}H_8$ compounds was low. Cyclopenta[*cd*]indene **16** was the only $C_{11}H_8$ compound identified. This indicates the occurrence of a 2-azulenylcarbene−1-azulenylcarbene rearrangement (Scheme 7). Singlet 2-azulenylcarbene is calculated to have an energy higher than those of the *Z* and *E* isomers of singlet 1-azulenylcarbene by 7 and 11 kcal/mol, respectively, so there is a thermodynamic driving force for the rearrangement. The calculated free energies make this rearrangement perfectly reasonable with an overall activation barrier of only ∼15 kcal/mol (Scheme 7). Species **32** may be formulated either as a planar carbene (**32a**) or a twisted six-membered cyclic allene (**32b**) like ^{1}**25a** and **25b** in Scheme 6.

Scheme 7. 2-Azulenylcarbene−1-Azulenylcarbene Rearrangement[a]



[a]Numbers in normal font are Gibbs free energies (Δ*G*) in kilocalories per mole at 873 K calculated at the B3LYP/6-31G** level, relative to ^{1}**18***E* = 0. Relative energies of transition states are indicated above the arrows. See the Supporting Information for an analogous scheme with electronic energies *E* and computational details.

Further experimental and computational investigation of these very complex systems is desirable.

■ CONCLUSION

The two reaction pathways of 1-azulenylcarbene **18**, routes a and b in Scheme 6, satisfactorily explain the formation of the thermal rearrangement products cyclopenta[*cd*]indene **16**, cyclobuta[*de*]naphthalene **6**, and benzofulvenallene **17** with modest calculated activation barriers of no more than 35 kcal/mol, which are easily achieved under FVP conditions. In addition, the formation of cyclopenta[*cd*]indene **16** via FVP of the precursor of 2-azulenylcarbene **30** indicates the occurrence of a 2-azulenylcarbene−1-azulenylcarbene rearrangement, with an overall activation barrier as low as 15 kcal/mol.

■ EXPERIMENTAL SECTION

Azulene-1-carbaldehyde Tosylhydrazone. Azulene-1-carbaldehyde (4.0 g, 25.6 mmol) was dissolved in 500 mL of a 2:1 mixture of dry ether and dry ethanol and treated with 4.76 g (25.6 mmol) of *p*-toluenesulfonyl hydrazine. The resulting mixture was stirred at rt under N_2 for 48 h. The solvent was then removed in vacuo, and the resulting solid was dried in vacuo at 10^{-2} hPa to yield 6.5 g (72%) of the tosylhydrazone as green crystals: mp 171−172 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.2 (s, 1H), 8.88 (d, *J* = 9.7 Hz, 1H), 8.46 (s, 1H), 8.40 (d, *J* = 9.7 Hz, 1H), 8.05 (d. *J* = 4.0 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.75 (t, *J* = 9.7 Hz, 1H), 7.40−7.29 (m, 5H), 2.29 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 144.4, 143.3, 143.2, 139.3, 137.0, 137.0, 136.3, 136.1, 135.6, 129.5, 127.5, 125.6, 125.5, 121.8, 118.7, 20.9; MS (EI) *m*/*z* (%) 324 (10), 169 (82), 156 (22), 142 (20), 140 (15), 139 (42), 115 (25), 91 (46), 65 (22), 39 (11); IR (KBr) 3180 s, 1590 s, 1575 s, 1495 m, 1460 m, 1390 s, 1350 s, 1330 s, 1285 s, 1165 vs, 905 s, 805 s, 765 s, 670 s cm^{-1}. The spectroscopic data are in agreement with those reported by Sander et al.[11] Anal. Calcd for $C_{18}H_{16}N_2SO_2$: C, 66.65; H, 4.97; N, 8.64. Found: C, 66.64; H, 4.85; N, 8.53.

Sodium Salt of Azulene-1-carbaldehyde Tosylhydrazone.[11] The foregoing hydrazone (2.0 g, 6.2 mmol) was dissolved in 100 mL of a 1:1 mixture of dry ether and dry methanol, and 150 mg (6.2 mmol) of dry NaH under ether was added under N_2. The resulting mixture was stirred under N_2 at rt for 24 h. Except for a couple of milliliters, the solvent was then removed in vacuo, and the remainder was allowed to crystallize at 0 °C; the solid was filtered under N_2 and dried at 10^{-2} hPa at 20 °C for 8 h to yield 1.2 g (56%) of the salt as green crystals, which were used as such in the pyrolyses.

5-(1-Azulenyl)tetrazole. A mixture of 1-cyanoazulene (3.06 g, 20 mmol), 1.43 g (22 mmol) of sodium azide, and 1.16 g (22 mmol) of ammonium chloride was stirred in 20 mL of dry DMF at 120 °C for 12 days under N_2. After the mixture had cooled, the solvent was removed in vacuo, and the remaining oil was treated with 150 mL of water and slowly acidified with HCl. The resulting precipitate was filtered, dissolved in a small amount of ethanol, chromatographed on silica gel, and eluted with ethanol. The first fraction consisted of unchanged 1-cyanoazulene (R_f = 0.75). The second fraction (R_f = 0.58) yielded the product (2.5 g, 64%) as violet crystals: mp 166−168 °C; ^{1}H NMR (DMSO-d_6) δ 9.63 (d, *J* = 9.8 Hz, 1H), 8.59 (d, *J* = 9.8 Hz, 1H), 8.50 (d, *J* = 4.0 Hz, 1H), 7.02 (d, *J* = 9.8 Hz, 1H), 7.58 (d, *J* = 9.8 Hz, 1H), 7.53 (d, *J* = 4.0 Hz, 1H), 7.48 (d, *J* = 9.8 Hz, 1H), 7.50 (very broad, 1H); ^{13}C NMR (DMSO-d_6) δ 152.3, 143.0, 138.8, 137.4, 136.4, 126.5, 126.3, 118.6, 110.1; IR (KBr) 3600−2000 (very broad), 1595 s, 1540 s, 1400 s, 1300 m, 1290 m, 1260 m, 1235 m, 1165 m, 1085 s, 910 m, 860 s, 775 s, 750 s cm^{-1}; MS (EI) *m*/*z* 153 ($M^{+\bullet} - HN_3$); MS (field desorption) *m*/*z* 196 ($M^{+\bullet}$). Anal. Calcd for $C_{11}H_8N_4$: C, 67.34; H, 4.11; N, 28.55. Found: C, 67.25; H, 4.08; N, 28.35.

5-(2-Azulenyl)tetrazole. A mixture of 2-cyanoazulene (2.0 g, 13.07 mmol), 936 mg (14.4 mmol) of sodium azide, and 762 mg (14.4 mmol) of ammonium chloride was stirred in 50 mL of dry DMF at 120 °C for 5 days under N_2. After the mixture had cooled, the solvent was removed in vacuo, and the remaining oil was treated with 50 mL of 2 N HCl. The resulting precipitate was filtered, dissolved in a small amount of ethanol, chromatographed on basic aluminum oxide, and eluted with ethanol. The first fraction consisted of the unchanged, violet-red 2-cyanoazulene (R_f = 0.75). The second fraction (R_f = 0.58) yielded the product (802 g, 31%) as dark blue crystals: mp 130−135 °C; ^{1}H NMR (DMSO-d_6) δ 8.46 (d, *J* = 9.6 Hz, 2H), 7.90 (t, *J* = 9.6 Hz, 1H), 7.26 (7, *J* = 9.6 Hz, 2H), 5.57 (very broad s, 1H); ^{13}C NMR (DMSO-d_6) δ 155.5 (s), 140.4 (m, *J* < 10 Hz), 138.1 (t, *J* = 10 and 154 Hz) 137.5 (d, *J* = 10 and 154 Hz), 135.7 (s), 124.1 (d, *J* = 10 and 157 Hz), 115.8 (d, *J* = 6 and 170 Hz); IR (film on KBr) 3700−2000 (very broad), 1660 s, 1585 m, 1400 s, 1470 m, 1390 s, 1090 s, 1055 s, 1025 m, 880 m, 765 s cm^{-1}; MS (field desorption) *m*/*z* (%) 197 (13, $M^{+\bullet}$ + 1), 196 (100, $M^{+\bullet}$). Anal. Calcd for $C_{11}H_8N_4$: C, 67.34; H, 4.11; N, 28.55. Found: C, 67.07; H, 4.15; N, 28.69.

Pyrolysis of Azulene-1-carbaldehyde Tosylhydrazone Sodium Salt. (a) A portion of 0.8 g of the salt described above was subjected to falling solid pyrolysis (FS-FVP)[12] at 600 °C at a pressure varying between 10^{-3} and 10^{-1} hPa over the course of 5 h. The resulting pyrolysate was distilled in a bulb-to-bulb manner at 90 °C and 10^{-3}–10^{-2} hPa to remove involatile components. The distillate was dissolved in $CDCl_3$ and examined by GC (SE 52, 160 °C, isothermally) and ^{1}H NMR spectroscopy. The following products were obtained: azulene (6%), 1*H*-cyclopenta[*cd*]indene **16** (13%), cyclobuta[*de*]naphthalene **6** (3%), and 1-methylazulene (15%).

(b) A small sample of the tosylhydrazone sodium salt was heated to 130 °C, and the vapors were fed through the pyrolysis apparatus at 10^{-3} hPa and condensed on a KBr target at 77 K for IR spectroscopy, which revealed an absorption at 2040 cm^{-1} ascribed to 1-(diazomethyl)azulene.

Pyrolysis of 5-(1-Azulenyl)tetrazole. A sample of 1 g of the solid, powdered tetrazole was subjected to FS-FVP[12] at 600 °C at a pressure varying between 10^{-3} and 10^{-1} hPa over the course of 60 min. The resulting products were examined by GC (SE52, 160 °C isothermally) and ^{1}H NMR spectroscopy and identified by comparison with the compounds isolated previously.[10] The following products were obtained: naphthalene (7%), azulene (20%), 1*H*-cyclopenta[*cd*]-indene **16** (11%), cyclobuta[*de*]naphthalene **6** (21%), and 1-cyanoazulene (40%). 1-Vinylideneindene **17** did not survive GC but was identified by its ^{1}H NMR signal at 5.43 ppm and its IR absorption at 1935 cm^{-1}.[10]

Pyrolysis of 5-(2-Azulenyl)tetrazole. (a) A sample of 500 mg of the solid, powdered tetrazole was subjected to FS-FVP at 600 °C at a pressure varying between 10^{-3} and 10^{-1} hPa over the course of 50 min. The resulting products were dissolved in $CDCl_3$ and examined by GC−MS (SE30, 160 °C isothermally) and ^{1}H NMR spectroscopy and identified by comparison with the products isolated previously.[10] The following products were obtained: naphthalene (9%), azulene (8%), 1*H*-cyclopenta[*cd*]indene **16** (5%), and 2-cyanoazulene (62%). There was no evidence of cyclobuta[*de*]naphthalene **6**.

(b) A small sample of 5-(2-azulenyl)tetrazole ws sublimed at 100 °C and pyrolyzed at 350 °C and 10^{-4} hPa. The products was condensed on a KBr target at 77 K for IR spectroscopy, which revealed an absorption at 2060 cm^{-1} ascribed to 2-(diazomethyl)azulene.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of pyrolysis products **6** and **16**, Schemes 3, 6, and 7 with electronic energies at 273.15 K, computational details, Cartesian coordinates, energies, and imaginary frequencies (where applicable) of calculated structures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00412.

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Notes

The authors declare no competing financial interest.

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