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$C_{15}H_{10}$ and $C_{15}H_{12}$ Thermal Chemistry: Phenanthrylcarbene Isomers and Phenylindenes by Falling Solid Flash Vacuum Pyrolysis of Tetrazoles

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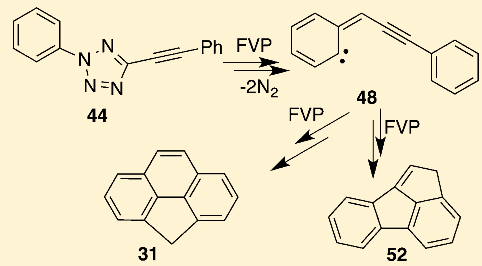
Supporting Information

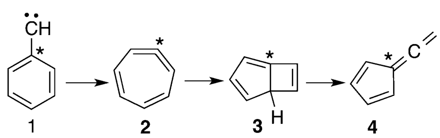
ABSTRACT: 2-Phenyl-5-(phenylethynyl)tetrazole **44** provides a new entry to the $C_{15}H_{10}$ energy surface. Flash vacuum pyrolysis of **44** using the falling solid flash vacuum pyrolysis (FS-FVP) method afforded cyclopenta[*def*]-phenanthrene **31** and cyclopenta[*jk*]fluorene **52** as the principal products. The products are explained in terms of the formation of *N*-phenyl-*C*-phenylethynylnitrile imine/(phenylazo)(phenylethynyl)carbene **45** and its cyclization to 3-(phenylethynyl)-3*H*-indazole **46b**. Pyrolytic loss of N_2 from **46b** generates $C_{15}H_{10}$ intermediate **48**. Cyclization of **48** to a dibenzocycloheptatetraene derivative and further rearrangements with analogies in the chemistry of phenylcarbene and the naphthylcarbenes leads to the final products. Similar pyrolysis of 2-phenyl-5-styryltetrazole **43** afforded 3-styrylindazole **58**, which on further pyrolysis eliminated N_2 to generate 3- and 2-phenylindenes **61** and **62** via $C_{15}H_{12}$ intermediates.



INTRODUCTION

The rich rearrangement chemistry of phenylcarbene[1] (Scheme 1) and the naphthylcarbenes[2] (Scheme 2) has been the subject of detailed investigations under both thermal and photochemical reaction conditions.

Scheme 1. Rearrangement of Phenylcarbene 1 to Cycloheptatetraene 2 and Fulvenallene 4[1]



The thermal interconversion of 2- and 1-naphthylcarbenes **5** and **9**, and their rearrangement to cyclobuta[*de*]naphthalene **10**, is summarized in Scheme 2.[3−5] DFT calculations indicated that the tricyclic cyclopropenes **6TS** and **8TS** are transition states.[6]

9-Phenanthrylcarbene **20** has been observed directly by ESR spectroscopy following photolysis of diazo compound **18**.[7] This carbene can be generated thermally by flash vacuum pyrolysis (FVP) of either **18** or the tetrazole **19**. Loss of N_2 from tetrazole **19** probably occurs via the 5*H* tautomer[8] to generate **18**. Thus, FVP of both **18** and **19** produced cyclobuta[*de*]-phenanthrene **21**, but in addition, a small amount of 4*H*-cyclopenta[*def*]phenanthrene **31** was also obtained (Scheme 3).[4]

A likely mechanism for the formation of **31** is illustrated in Scheme 3. Cyclopropene **22** is a known intermediate, which has been formed by intramolecular addition of the photochemically generated arylcarbene **23** to the acetylene moiety.[9] Compound **22** has also been generated in solution by photolysis of the tosylhydrazone salt **26** and trapped by Diels−Alder addition of cyclopentadiene, butadiene, and furan to the strained cyclopropene C═C bond.[10,11] Phenanthrylcarbene **20**, formed by rearrangement of the dibenzocycloheptatrienylidene **25** or cycloheptatetraene **24** by thermolysis of **26** at 125 °C in benzene solution, was trapped by addition to benzene, forming 9-(7-cycloheptatrienyl)phenanthrene.[10] The rearrangement of **24** or **25** to **22** takes place at −60 °C upon photolysis of **26**. The top row in Scheme 3 connecting **20**, **22**, **24**, and **25** is analogous to the rearrangements of the naphthylcarbenes[3−5] (Scheme 2). The reaction sequence **28** → **29** → **30** is a normal phenylcarbene rearrangement, and the final cyclization to **31** is expected to be rapid and highly exothermic.[12] It is worth noting that attempts to observe 4-phenanthrylcarbene (from 4-diazomethylphenanthrene) by ESR spectroscopy failed, probably because of its cyclization to **31** under the photolysis conditions.[7]

The postulated carbene−carbene rearrangement **25** → **27** → **28** would pass through the strained intermediate or transition state **27**. We will refer to this type of reaction as a *ring interchange*. In fact, there is excellent evidence for carbene−carbene rearrangements via strained cyclopropenes of this type.[4,13] Two such examples are shown in Scheme 4. Carbene **33** has a triplet ground state,[14] but the excited singlet[15] and the

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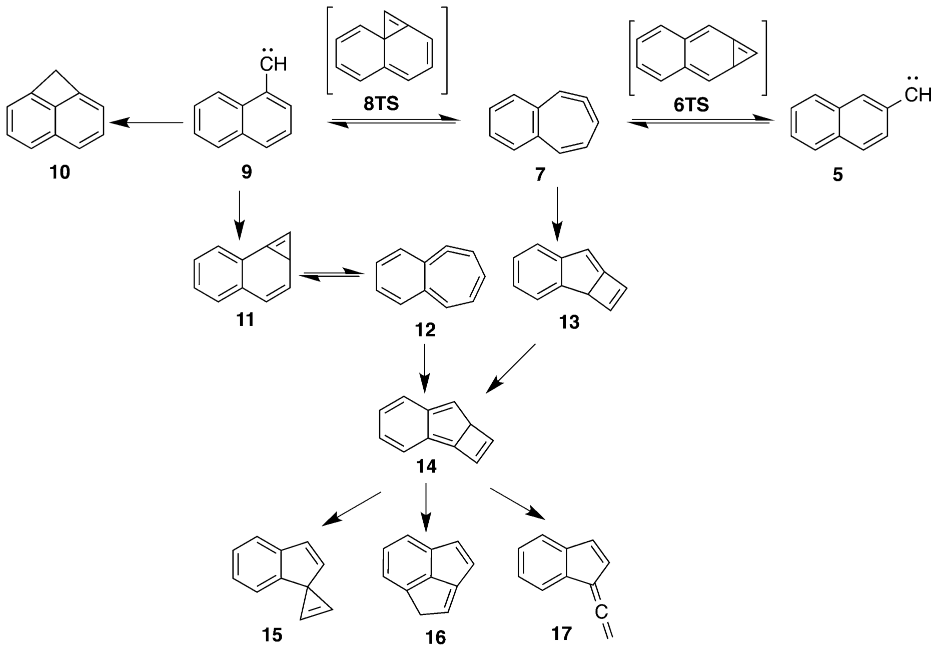
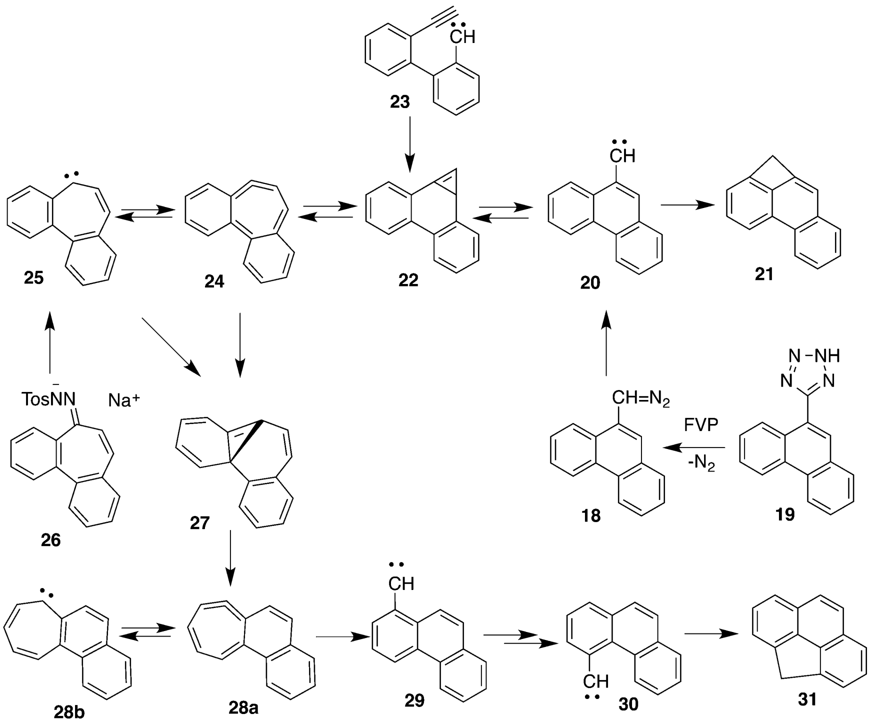
Scheme 2. Rearrangements of the Naphthylcarbenes 5 and 9 to 10, 15, 16, and 17



Scheme 3. Phenanthrylcarbene Rearrangements



excited triplet states are also known.[16] Generated by FVP of diazo compound **32**, it yields two products, **34** and **38**.[4] The analogous rearrangement of **40** to **31** was observed upon FVP of diazodibenzocycloheptene **39** (Scheme 4).[13] Both reactions require a ring interchange via **35** or **41**. Early SCF calculations indicated that the tetracyclic cyclopropene intermediate **35** lies only ~23 kcal/mol above **33**[4] (i.e., these reactions are perfectly feasible under FVP conditions).

The importance of phenylcarbene **1** and fulvenallene **4** in the formation of polycyclic aromatic hydrocarbons (PAHs) in combustion processes has received much attention recently.[17] The involvement of higher arylcarbenes and rearrangements of arylcarbenes in PAH formation seem very likely. However, there is no knowledge of this in the literature, and the mechanisms of higher PAH formation are poorly understood.[18] $C_{15}H_{10}$ isomer cyclopenta[*def*]phenanthrene **31** was identified recently as a product of pyrolysis of catechol, which was used as a model for pyrolysis of solid fuels.[19] Other methylene-bridged PAHs were also characterized.[19] Indene figures prominently in models of combustion and pyrolysis reactions and the formation of PAHs,[20] and 2-phenylindene has been detected in the pyrolysis oil from pine sawdust intended for use as

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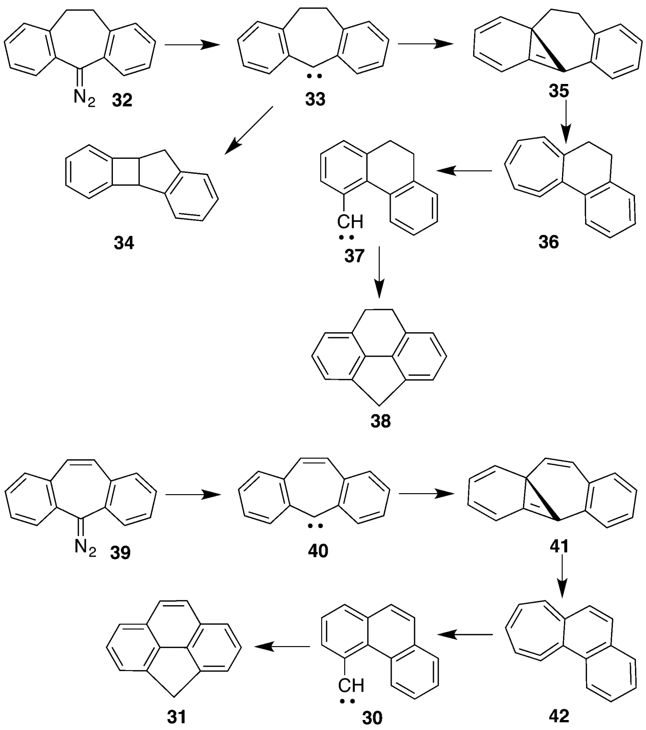
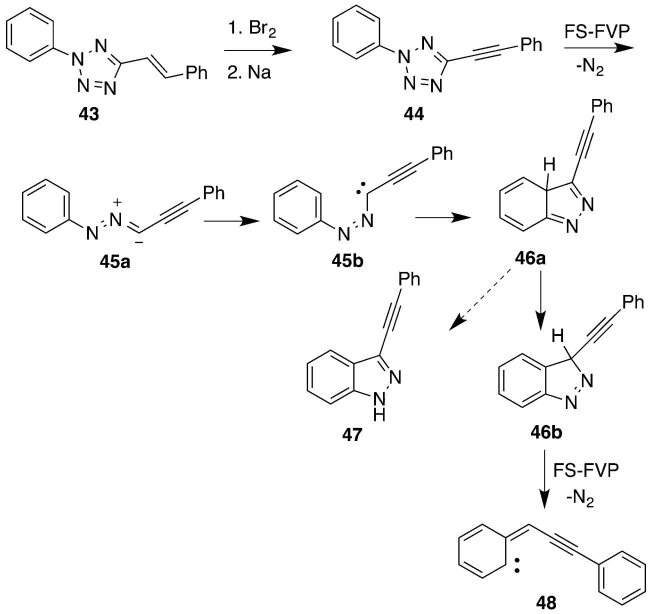
Scheme 4. Dibenzo[a,d]cyclohepten-5-ylidene Rearrangements;[4,31] Cyclic Carbenes Isomeric with the Allenes 36 and 42 are Omitted for the Sake of Simplicity



Scheme 5. Synthesis and Pyrolysis of 2-Phenyl-5-(phenylethynyl)tetrazole 44



biodiesel[21] and in the pyrolysis of 1-phenyltetralin investigated as a model for lignins responsible for coal formation.[22] Here, we report new results on the pyrolytic formation and rearrangements of the $C_{15}H_{10}$ phenanthrylcarbene isomers and $C_{15}H_{12}$ phenylindene isomers.

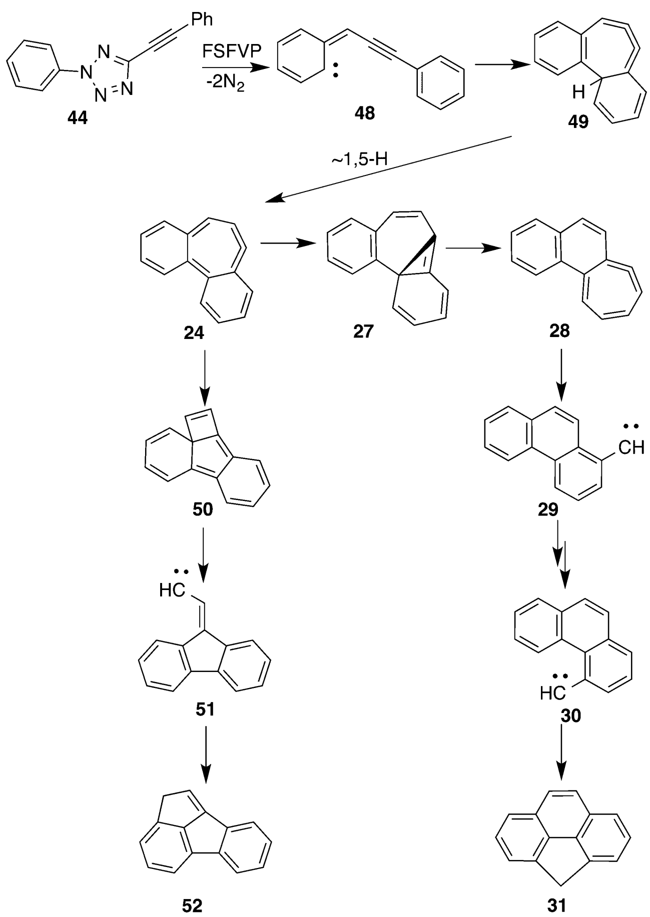
■ RESULTS AND DISCUSSION

1. 2-Phenyl-5-(phenylethynyl)tetrazole 44. 2-Phenyl-5-(phenylethynyl)tetrazole **44** provides a new entry to the $C_{15}H_{10}$ energy surface. This compound was prepared by the straightforward addition of bromine to styryltetrazole **43** followed by elimination of HBr with sodium (Scheme 5). Because of the low volatility of **44**, we applied the falling solid flash vacuum pyrolysis (FS-FVP) method.[23] Using this technique, the solid tetrazole was pyrolyzed at 400−500 °C at a dynamic pressure between 10^{-3} and 10^{-1} hPa.

As is common for 2,5-disubstituted tetrazoles,[24] the pyrolysis of **44** should result in the elimination of N_2 with the formation of nitrile imine **45a**. Several mesomeric structures and conformations of this compound can be formulated,[24] including the Z-conformer of the carbene canonical structure **45b**, which can now cyclize to indazole **46a** in a 6-electron electrocyclization analogous to previously reported cyclizations of nitrile imines.[24,25] A 1,5-H shift affords 3H-indazole **46b** (Scheme 5). Further isomerization leads to indazole **47**, but this reaction may not be unimolecular. In this event, the ^{1}H NMR and mass spectra clearly indicated that **47** was present in the products of pyrolysis at 400 °C, but at 500 °C, it had disappeared. This is ascribed to tautomer **46b** eliminating a second molecule of N_2, thereby forming carbene **48** and entering the $C_{15}H_{10}$ energy surface.

The main products of the FS-FVP reaction at 500 °C were cyclopenta[def]phenanthrene **31** and cyclopenta[jk]fluorene **52** in yields of 30 and 60%, respectively (Scheme 6). Carbene **48** may cyclize to the cycloheptatetraene intermediate **49**. A 1,5-H shift in **49** can yield the more stable isomer **24**, which can now rearrange to **28** via strained tetracyclic cyclopropene **27**,

Scheme 6. New $C_{15}H_{10}$ Intermediates



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which was discussed above in connection with Schemes 3 and 4. Further rearrangement of **28** to **31** is a straightforward phenylcarbene-type[1] rearrangement (Scheme 6).

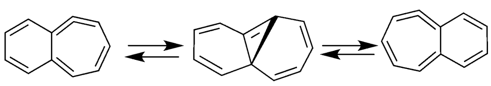
Cyclic allene **24** may also undergo a transannular cyclization similar to that of cycloheptatetraene (**2** → **3**, Scheme 1)[1] and the naphthylcarbenes[3−6] (Scheme 2); this will lead to compound **50** (Scheme 6). Further ring opening to **51** and cyclization of **51** to **52** are completely analogous to the reactions taking place on the naphthylcarbene energy surface[27] (compare Schemes 2 and 6). Thus, the products of the FS-FVP of **44** are readily explained in terms of known types of processes.[1,3−6,27]

It is instructive to consider some known, calculated activation barriers for the types of rearrangements put forward here. The ring expansion of singlet phenylcarbene **1** to cycloheptatetraene **2** (Scheme 1) via bicyclo[4.1.0]hepta-2,4,7-triene has a barrier of 15−20 kcal/mol.[1,26] The transannular cyclization to **3** is the highest barrier for the ring contraction to fulvenallene **4**, ~46 kcal/mol at the B3LYP/6-31G* level.[1] Both reactions take place on FVP in our apparatus at 600 °C and above.[1]

The barrier for interconversion of the singlet naphthylcarbenes **9** and **5** depicted in Scheme 2 is ~24 kcal/mol at the B3LYP/6-31G** level.[6,27] For the cyclization to cyclobuta[*de*]-naphthalene **10** it is almost the same, 25 kcal/mol,[6,27] and both processes take place very easily under FVP conditions.[3,4] Nonaromatic cycloheptatetraene **12** (Scheme 2) lies only ~15 kcal/mol higher than aromatic **7**.[6,27] The barriers for the formation of **13−17** were evaluated recently in the context of the azulenylcarbene rearrangements, and the highest barrier is ~44 kcal/mol relative to the singlet state of the *E*-isomer of 1-naphthylcarbene **9**.[27] The formation of **15−17** is known to take place on FVP at 600 °C and above.[4,5]

The reactions become a little more complicated when we consider ring interchange reactions, such as **24** → **27** → **28** (Schemes 3 and 6). Early force field − SCF calculations indicated that tetracyclic cyclopropene **35**, formed from 5-diazo-9,10-dihydrodibenzo[*a,d*]cycloheptene **32**, lies ~23 kcal/mol above carbene **33** (Scheme 4).[4] The tricyclic cyclopropene intermediate **53** in the ring-interchange in the $C_{11}H_8$ system (**12**, Scheme 7) was calculated to lie 36 kcal/mol above **12**.[6]

Scheme 7. Ring Interchange in $C_{11}H_8$



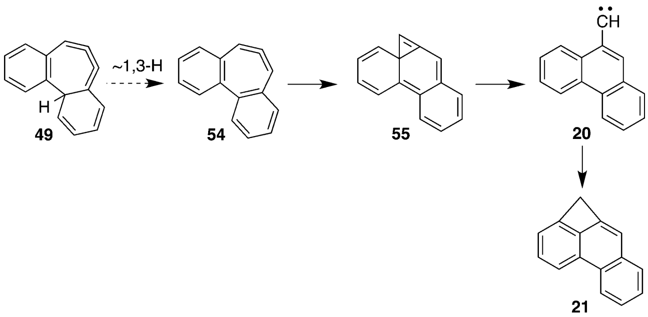
12 53 12

Accordingly, the interconversions of **24** and **28** via **27** in Scheme 3 and Scheme 6 appear to be perfectly reasonable under the FVP conditions, where experience shows that activation energies on the order of 50 kcal/mol are readily achievable.

The ratios of products **31** and **52** in Scheme 6 (1:6 at 400 °C and 1:2 at 500 °C) indicate that the transannular cyclization **24** → **50** is faster than the ring interchange reaction **24** → **27** → **28**.

It should be noted that one could also have expected a 1,3-H shift (which can also be formulated as a 1,7-H shift) in cycloheptatetraene **49**, yielding **54** and then, in principle, 9-phenanthrylcarbene **20** (Scheme 8). However, this process can be excluded because the known product of 9-phenanthrylcarbene, cyclobuta[*de*]phenanthrene **21** (Scheme 3), could not be detected as a product of the FS-FVP of **44** by either GC or

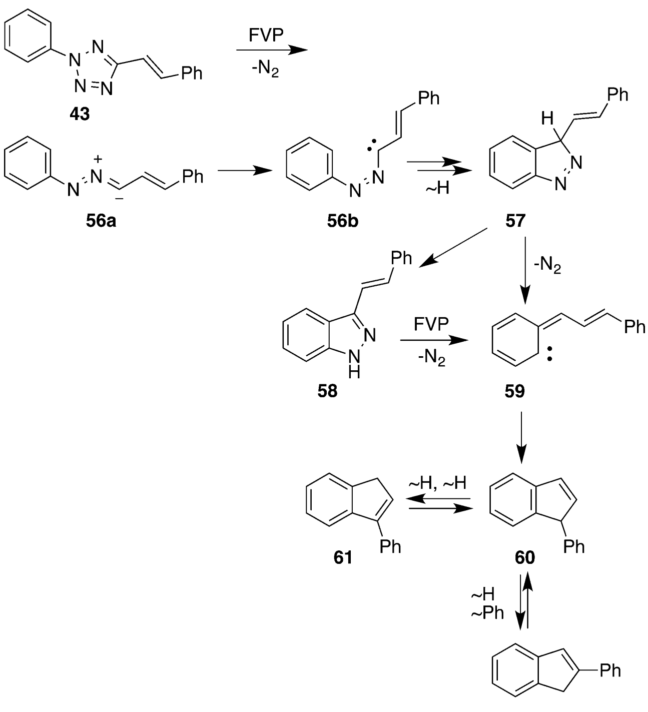
Scheme 8. Unobserved 1,3-H Shift in 49



NMR spectroscopy (the NMR spectra of **21** obtained by FVP of **19** are shown in the Supporting Information for comparison). Thus, the 1,5-H shift (Scheme 6) is energetically preferred over the 1,3-H shift (Scheme 8) in agreement with the Woodward−Hoffmann rules, even though the 1,3-shift in **49** should be possible as a pseudopericyclic reaction because of the presence of orthogonal orbitals in the 1,2,3-triene moiety.

2. 2-Phenyl-5-styryltetrazole 43. 5-Styryltetrazole **43** was also subjected to FS-FVP under the same conditions used for **44**. In this case, indazole **58** (Scheme 9) was isolated in 69%

Scheme 9. 3-Styrylindazole 58 and 3- and 2-Phenylindenes 61 and 62 from FVP of 2-Phenyl-5-styryltetrazole 43



yield and fully characterized when using a pyrolysis temperature of 360 °C. Further FS-FVP of **43** at 400−800 °C afforded increasing amounts of 3- and 2-phenylindenes **61** and **62** and decreasing amounts of **58**. At 800 °C, a nearly 1:1 mixture of 3- and 2-phenylindenes **61** and **62** was obtained in 89% yield, and only ~7% of **58** remained (Scheme 9). Unlike ethynyl analogue **48** in Scheme 6, carbene intermediate **59** can cyclize to 1-phenylindene **60**, which then isomerizes to the more stable, conjugated 3- and 2-phenylindenes **61** and **62** by means of sequential 1,5-H and 1,5-Ph shifts (Scheme 9).

It is known that 3- and 2-phenylindenes interconvert thermally; von Braun and Manz observed the isomerization of 3-phenylindene to 2-phenylindene (but not the reverse) upon passing the vapors in a stream of CO_2 over pumice in a dark-red glowing tube.[28] Koelsch and Johnson confirmed the phenyl migration from the 1- to the 2-position in the pyrolysis of some polysubstituted phenylindenes in a steam of N_2 at 450−490 °C.[29] Miller and Boyer determined the activation parameters for the hydrogen shifts in 1-phenylindene through two sequential 1,5-H shifts to yield 3-phenylindene in a diphenyl ether solution at 140−160 °C as $\Delta H^‡$ = 33 kcal mol^{-1} and $\Delta S^‡$ = −2.3 cal K^{-1} mol^{-1}.[30] In substituted 1-phenylindenes (e.g., 1,1-diphenylindene and 1-methyl-1-phenylindene), they concurred with the previous authors[28,29] that phenyl migration takes place specifically to the 2-position and reported an activation enthalpy of ∼28 kcal mol^{-1} and a strongly negative activation entropy $\Delta S^‡$ = −25 to −27 cal K^{-1} mol^{-1} for the phenyl migration in solution at an average temperature of 265 °C.[30] This translates to a free energy of activation for phenyl migration of ∼42 kcal mol^{-1}. These values are very similar to those calculated for the corresponding interconversion of 3- and 2-cyanoindenes (33 kcal mol^{-1} for 1,5-H migration; 46 kcal mol^{-1} for 1,5-CN migration starting from 1-cyanoindene)[31] and are in line with the observation that high temperatures are required for equilibration of the 2- and 3-isomers. Brown, Eastwood, and Jackman obtained a mixture of 2- and 3-phenylindenes in a ratio of 12:7 upon FVP of phenyl(*o*-tolyl)acetylene at 790 °C. Similar FVP of 3-phenylindene at 710 °C also afforded a mixture of 2- and 3-phenylindenes in a ratio of 12:7, and 2-phenylindene at 700 °C afforded a mixture of 2- and 3-phenylindenes in a ratio of 17:8.[32] As mentioned above, we obtained a nearly 1:1 ratio at 800 °C.

■ CONCLUSION

Falling solid flash vacuum pyrolysis (FS-FVP) of **44** proceeds via *N*-phenyl-*C*-(phenylethynyl)nitrile imine/(phenylazo)-(phenylethynyl)carbene **45** and 3-(phenylethynyl)-3*H*-indazole **46b** to generate carbene **48** as the first $C_{14}H_{10}$ intermediate. Two series of pericyclic reactions yields cyclopenta[*def*]-phenanthrene **31** and cyclopenta[*jk*]fluorene **52** as final products. An analogous but much simpler reaction is the formation of 3-styrylindazole **58**, 3-phenylindene **61**, and 2-phenylindene **62** from 2-phenyl-5-styryltetrazole **43**.

All of the rearrangement mechanisms depicted in Schemes 3, 4, 6, 7, and 9 are estimated to have activation barriers <50 kcal/mol and therefore to be perfectly accessible under flash vacuum pyrolysis conditions in the 500−800 °C temperature range.

■ EXPERIMENTAL SECTION

The apparatus and procedure for falling solid flash vacuum pyrolysis (FS-FVP) have been described.[23] All HRMS measurements were carried out using a conventional double-focusing sector mass spectrometer of Mattauch−Herzog geometry. Electron ionization at 70 eV (EI) and field desorption (FD) is indicated where appropriate.

Synthesis of 2-Phenyl-5-styryltetrazole 43. This compound was prepared according to the procedure of Ito et al.;[33] mp 88−90 °C [lit.[33] 90 °C].

Synthesis of 2-Phenyl-5-(phenylethynyl)tetrazole 44. *2-Phenyl-5-(2-phenyl)-1,2-dibromoethyl)tetrazole.* Bromine (4.5 g; 28 mmol) in 10 mL of glacial acetic acid was added slowly to a stirred solution of **43** (700 mg; 2.82 mmol) in 50 mL of glacial acetic acid containing a trace catalytic amount of LiBr. The resulting mixture was allowed to stand for 6 h at RT, and the precipitated product was filtered and dried in vacuo at 10^{-2} hPa to yield 1.0 g (87%) of 2-phenyl-5-(2-phenyl-1,2-dibromoethyl)tetrazole as light rosa colored crystals; mp 173−175 °C. ^{1}H NMR ($CDCl_3$): δ 8.19−8.16 (m, 2H), 7.60−7.38 (m, 8H), 5.95 (d, J = 11.8 Hz, 1H), 5.87 (d, J = 11.8 Hz, 1H).

^{13}C NMR (DMSO-d_6): 165.9, 138.8, 135.7, 130.6, 130.2, 129.1, 128.6, 128.3, 119.9, 53.3, 41.3. IR (KBr/cm^{-1}): 3070 w, 2995 m, 1600 m, 1500 s, 1485 s, 1470 s, 1455 s, 1210 s, 1180 s, 1140 s, 1000 s, 790 s, 680 s. MS (FD) m/z: 301 ([M − ^{79}Br − H]$^+$, 25%), 299 ([M − ^{81}Br − H]$^+$, 28), 221 (10), 220 (70), 219 (15), 115 (5), 91 (100). Anal. Calcd for $C_{15}H_{12}N_4Br_2$: C, 44.11; H, 2.96; N, 13.76%. Found: C, 44.04; H, 2.78; N, 13.48%.

2-Phenyl-5-(phenylethynyl)tetrazole 44. A solution of 2-phenyl-5-(2-phenyl-1,2-dibromoethyl)tetrazole (800 mg; 2 mmol) in 10 mL of dry *tert*-butanol was added slowly to a stirred, boiling solution of 200 mg (8.6 mmol) of Na in 30 mL of dry *tert*-butanol. The resulting mixture was refluxed for another 30 min, cooled to RT, and 10 mL of water was added slowly with stirring. This mixture was evaporated to dryness in vacuo; the residue was taken up in diethyl ether, and the solution was dried over $MgSO_4$. Filtering and removal of the ether in vacuo afforded 350 mg (73%) of white crystals; mp 131−133 °C after recrystallization from petroleum ether. ^{1}H NMR ($CDCl_3$): δ 8.15−8.12 (m, 2H), 7.66−7.36 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 151.1 (C), 136.4 (C), 132.1 (CH), 12.9 (CH), 129.8 (CH), 129.6 (CH), 128.4 (CH), 120.7 (C), 119.7 (CH), 94.5 (C), 75.9 (C). IR (KBr/cm^{-1}): 3050 w, 2240 s, 1600 s, 1515 s, 1495 m, 1210 s, 1100 s, 1000 s, 760 s, 705 s, 690 s, 680 s. MS (FD) m/z: 246 (M$^{+\cdot}$). Anal. Calcd for $C_{15}H_{10}N_4$: C, 73.16; H, 4.10; N, 22.75%. Found: C, 73.16; H, 3.91; N, 22.70%.

Pyrolysis of 2-Phenyl-5-(phenylethynyl)tetrazole 44. (a) A sample of 250 mg of the solid, powdered tetrazole was subjected to FS-FVP at 500 °C at a pressure varying between 10^{-3} and 10^{-1} hPa in the course of 60 min. The resulting products were examined by GC (SE52, 200 °C isothermally) and ^{1}H NMR spectroscopy and identified by comparison with the compounds isolated previously.[4,34] The following products were obtained: 9*H*-cyclopenta[*def*]phenanthrene **31**, 30%; 2*H*-cyclopenta[*jk*]fluorene **52**, 60%. Data for 9*H*-cyclopenta-[*def*]phenanthrene **31** as follows. ^{1}H NMR ($CDCl_3$): δ 7.88−7.66 (m, 8H), 4.36 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 141.8, 138.4, 127.9, 127.2, 125.3, 122.5, 121.2, 37.4 (t, J_H = 131 Hz).

The data are in agreement with the literature,[4,5] and the identity of the compound was confirmed by coinjection of an authentic sample on SE30 and SE52 GC columns.

Data for 2*H*-cyclopenta[*jk*]fluorene **52** as follows. ^{1}H NMR ($CDCl_3$): δ 7.72−7.34 (m, 7H), 6.77 (t, J = 1.4 Hz, 1H), 4.07 (d, J = 1.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 147.4, 142.8, 135.3, 134.9, 130.3, 127.45, 127.4, 126.5, 126.3, 125.8, 125.4, 124.8, 122.5, 118.3, 46.0 (dt, J_H = 9 and 130 Hz). MS (EI) m/z: 190 (M$^{+\cdot}$, 100%), 189 (70), 188 (11), 187 (17), 163 (10), 95 (10), 94 (10). HRMS (EI) m/z: 190.0767; calcd for $C_{15}H_{10}$: 190.0782. The data are in agreement with the literature.[34]

(b) A sample of 100 mg of the tetrazole was pyrolyzed at 400 °C. ^{1}H and mass spectra of the product indicated the presence of a mixture of 3-(phenylethynyl)indazole **47**, cyclopenta[*def*]phenanthrene **31**, and cyclopenta[*jk*]fluorene **52** at a ratio of 1:1:6, which was separated by flash chromatography on silica gel.

Data for 3-(phenylethynyl)indazole **47** as follows. ^{1}H NMR ($CDCl_3$): δ 10.5 (broad s, NH), 7.1−7.6 (m). MS (EI) m/z: 218 (M$^{+\cdot}$, 100%), 190 (11), 189 (35), 109 (6), 89 (6), 69 (5). HRMS (EI) m/z: 218.0840; calcd for $C_{15}H_{10}N_2$: 218.08439. Anal. Calcd for $C_{15}H_{10}N_2$: C, 82.55; H, 4.62; N, 12.84%. Found: C, 82.61; H, 4.59; N, 12.76%.

Pyrolysis of 2-Phenyl-5-styryltetrazole 43. Samples of 100−409 mg (0.27−1.65 mmol) of **43** were pyrolyzed in the range of 360−800 °C/10^{-3} hPa.

(a) Pyrolysis of 409 mg (1.65 mmol) of tetrazole **43** at 360 °C afforded almost pure 3-styrylindazole **58**. Recrystallization from $CHCl_3$ yielded 249 mg (69%) of 3-styrylindazole **58** as white needles; mp 174−175 °C. ^{1}H NMR ($CDCl_3$): δ 10.8 (broad s, NH), 8.02 (d, J = 17 Hz, 1H), 7.65 (d, J = 17 Hz, 1H), 7.1−7.6 (m, 9 H). ^{13}C NMR

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J. Org. Chem. XXXX, XXX, XXX−XXX

($CDCl_3$; coupling pattern determined by off-resonance decoupling): δ 141.9 (C), 141.0 (C), 136.9 (C), 129.0 (CH), 128.4 (CH), 127.3 (CH), 126.1 (CH), 126.0 (CH), 120.55 (CH), 120.5 (CH), 120.45 (C), 120.4 (CH), 110.2 (CH). MS m/z: 220 ($M^{+\cdot}$, 48%), 219 (100), 109 (8), 108 (9), 77 (6). IR (KBr): 3260 (broad), 1620 s, 1600 m, 1500 s, 1480 m, 1460 m, 1350 s, 1280 s, 1240 s, 1060 s, 960 s, 770 s, 740 s, 690 s cm^{-1}. Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72%. Found: C, 81.86; H, 5.39; N, 12.66%.

(b) At 400−700 °C, mixtures of decreasing amounts of **58** and increasing amounts of 2- and 3-phenylindenes **61** and **62** were obtained. At 800 °C, an ~1:1 mixture of **61** and **62** was obtained in 89% yield (80 mg from 116 mg (0.47 mmol) of **43**). These compounds were identified by comparison of the GC data and ^1H NMR spectra with those of authentic materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of pyrolysis products **21**, **31**, **52**, **58**, **61**, and **62**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01007.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Kvaskoff, D.; Lüerssen, H.; Bednarek, P.; Wentrup, C. *J. Am. Chem. Soc.* **2014**, *136*, 15203.

(2) (a) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353. (b) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 175.

(3) Becker, J.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 190.

(4) Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. J. *Tetrahedron* **1985**, *41*, 1601.

(5) Also see related work using pyrolysis of methoxy(trimethylsilyl) methylnaphthalenes and -phenanthrenes as carbene sources: Engler, T. A.; Shechter, H. *J. Org. Chem.* **1999**, *64*, 4247.

(6) Xie, Y.; Schreiner, P. R.; Schleyer, P.; von, R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1997**, *119*, 1370.

(7) Roth, H. D.; Hutton, R. S. *Tetrahedron* **1985**, *41*, 1567.

(8) 5*H*-tautomer of tetrazole: Wong, M. W.; Leung-Toung, R.; Wentrup, C. *J. Am. Chem. Soc.* **1993**, *115*, 2465.

(9) Mykytka, J. P.; Jones, W. M. *J. Am. Chem. Soc.* **1975**, *97*, 5933.

(10) Coburn, T. T.; Jones, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5218.

(11) Chloro- and methylthio-derivatives of **22** have also been generated and trapped with methanethiol: Billups, W. E.; Lin, L. P.; Chow, W. Y. *J. Am. Chem. Soc.* **1974**, *96*, 4026.

(12) The cyclization of **23** to **24** is analogous to the cyclization of 2-biphenylylcarbene to fluorene: (a) Regimbald-Krnel, M. J.; Wentrup, C. *J. Org. Chem.* **2013**, *78*, 8789. (b) Monguchi, K.; Itoh, T.; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **2004**, *126*, 11900.

(13) Tomioka, H.; Kobayashi, N. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 327.

(14) Moritani, I.; Murahashi, S.-I.; Nishino, M.; Yamamoto, Y.; Itoh, K.; Mataga, N. *J. Am. Chem. Soc.* **1967**, *89*, 1259.

(15) Wang, J.; Zhang, Y.; Kubicki, J.; Platz, M. S. *Photochem. Photobiol. Sci.* **2008**, *7*, 552.

(16) Akiyama, K.; Suzuki, A.; Morikuni, H.; Tero-Kubota, S. *J. Phys. Chem. A* **2003**, *107*, 1447.

(17) (a) Hansen, N.; Kasper, T.; Klippenstein, S. J.; Westmoreland, P. R.; Law, M. E.; Taatjes, C. A.; Kohse-Höinghaus, K.; Wang, J.; Cool, T. A. *J. Phys. Chem. A* **2007**, *111*, 4081. (b) da Silva, G.; Bozzelli, J. W. *J. Phys. Chem. A* **2009**, *113*, 12045. (c) da Silva, G.; Cole, J. A.; Bozzelli, J. W. *J. Phys. Chem. A* **2009**, *113*, 6111. (d) Cavallotti, C.; Derudi, M.; Rota, R. *Proc. Combust. Inst.* **2009**, *32*, 115. (e) Li, Y. Y.; Zhang, L. D.; Tian, Z.; Yuan, T.; Wang, J.; Yang, B.; Qi, F. *Energy Fuels* **2009**, *23*, 1473 and references in these papers.

(18) (a) Trogolo, D.; Maranzana, A.; Ghigo, G.; Tonachini, G. *J. Phys. Chem. A* **2014**, *118*, 427. (b) Liu, P.; Lin, H.; Yang, Y.; Shao, C.; Guan, B.; Huang, Z. *J. Phys. Chem. A* **2015**, *119*, 3261. (c) Parker, D. S. N.; Kaiser, R. I.; Bandyopadhyay, B.; Kostko, O.; Troy, T. P.; Ahmed, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 5421.

(19) Thomas, S.; Poddar, N. B.; Wornat, M. J. *Polycyclic Aromat. Compd.* **2012**, *32*, 531.

(20) (a) da Silva, G.; Bozzelli, J. W. *J. Phys. Chem. A* **2009**, *113*, 8971. (b) Zhang, F.; Kaiser, R. I.; Kislov, V. V.; Mebel, A. M.; Golan, A.; Ahmed, M. *J. Phys. Chem. Lett.* **2011**, *2*, 1731. (c) Parker, D. S. N.; Zhang, F.; Kaiser, R. I.; Kislov, V. V.; Mebel, A. M. *Chem.—Asian J.* **2011**, *6*, 3035. (d) Cavallotti, C.; Polino, D.; Frassoldati, A.; Ranzi, E. *J. Phys. Chem. A* **2012**, *116*, 3313. (e) Raj, A.; Prada, I. D. C.; Amer, A. A.; Chung, S. H. *Combust. Flame* **2012**, *159*, 500. (f) Yuan, W.; Li, Y.; Dagaut, P.; Yang, J.; Qi, F. *Combust. Flame* **2015**, *162*, 3. (g) Lu, M.; Mulholland, J. A. *Chemosphere* **2001**, *42*, 625. (h) Badger, G. M.; Kimber, R. W. L. *J. Chem. Soc.* **1960**, 2746. (i) Wentrup, C.; Winter, H.-W.; Kvaskoff, D. *J. Phys. Chem. A* **2015**, *119*, 6370−6376.

(21) Huang, Y.; Wei, L.; Julson, J.; Gao, Y.; Zhao, Z. *J. Anal. Appl. Pyrolysis* **2015**, *111*, 148.

(22) Wilshire, J. F. K. *Aust. J. Chem.* **1962**, *15*, 538.

(23) (a) Wentrup, C.; Becker, J.; Winter, H.-W. *Angew. Chem., Int. Ed.* **2015**, *54*, 5702. (b) Wentrup, C. *Aust. J. Chem.* **2014**, *67*, 1150.

(24) (a) Bégué, D.; Qiao, G. G.; Wentrup, C. *J. Am. Chem. Soc.* **2012**, *134*, 5339. (b) Bégué, D.; Wentrup, C. *J. Org. Chem.* **2014**, *79*, 1418.

(25) Wentrup, C.; Damerius, A.; Reichen, W. *J. Org. Chem.* **1978**, *43*, 2037.

(26) (a) 16.5 kcal/mol at the CASPT2(8,8)/6-31G*//CASSCF(8,8)/6−32G* level: Karney, W. L.; Borden, W. T. *Adv. Carbene Chem.* **2001**, *3*, 205−250. (b) 14.8 kcal/mol at the B3LYP/6-311+G** level: Geise, C. M.; Hadad, C. M. *J. Org. Chem.* **2002**, *67*, 2532. (c) 20.7 kcal/mol at the B3LYP/6-31G* + ZPVE level, see ref 1.

(27) Kvaskoff, D.; Becker, J.; Wentrup, C. *J. Org. Chem.* **2015**, *80*, 1530.

(28) Braun, J. v.; Merz, G. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 1059.

(29) Koelsch, C. F.; Johnson, P. R. *J. Am. Chem. Soc.* **1943**, *65*, 567.

(30) Miller, L. L.; Boyer, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 650.

(31) Wentrup, C. *Aust. J. Chem.* **2013**, *66*, 852.

(32) Brown, R. F. C.; Eastwood, F. W.; Jackman, G. P. *Aust. J. Chem.* **1977**, *30*, 1757.

(33) Ito, S.; Tanaka, Y.; Kakehi, A.; Kondo, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1920.

(34) Luger, P.; Tuchscherer, C.; Große, M.; Rewicki, D. *Chem. Ber.* **1976**, *109*, 2596.

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J. Org. Chem. XXXX, XXX, XXX−XXX