

Characterization of Cured Polystyrylpyridine by Model Compounds*

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Synopsis

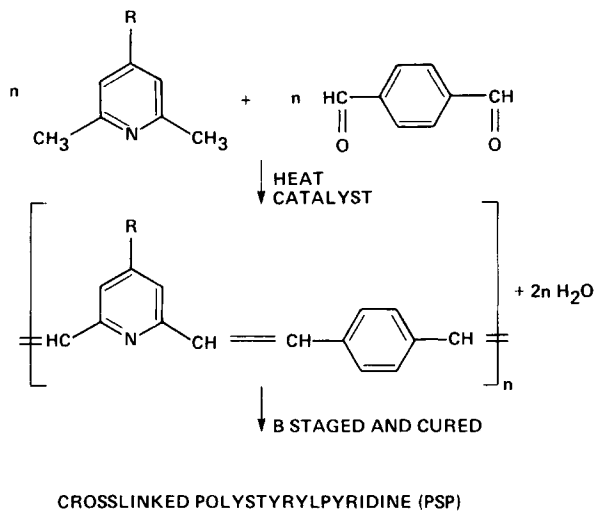
The crosslinking or curing reaction of polystyrylpyridine (PSP) has been studied by means of thermal reactions of its model compounds. Compounds 2,6-distyrylpyridine, 4-stilbazole (4-styrylpyridine), and deuterated 4-stilbazole were pyrolyzed at 200–325°C both in air and under vacuum in a sealed tube. The major pyrolysis products were diarylethane and stilbene, and were characterized by gas chromatography-mass spectrometry. Major dimeric products were naphthalene or quinoline derivatives. Mechanisms for the pyrolysis are suggested, and a crosslinked structure for cured PSP is proposed based on the thermal reaction products of model compounds.

INTRODUCTION

It has been reported¹ that a fire-resistant composite resin prepolymer was synthesized from the condensation reaction of methylated derivatives of pyridine and aromatic dialdehyde (Fig. 1). After the prepolymer was cured by heating first at 200°C for 3 hr and then at 250°C for 2 hr, and finally postcured at 250°C for 16 hr or at 300°C for 3 hr, a crosslinked polystyrylpyridine (PSP) resin was obtained. The cured PSP resins have very good thermal stability and anti-flammability properties. A high char yield was obtained by pyrolysis in a non-oxidative atmosphere, and the residue had good mechanical integrity.^{2,3} The structure of cured PSP has not been determined, but the crosslinking reaction presumably involves the aliphatic —CH=CH— units even though the infrared (IR) spectrum of cured PSP does not indicate the type of crosslinking reactions involved in the curing. As the cured PSP resin is not soluble in organic solvents, its structure is not easily studied by conventional methods. To clarify the chemical structure of cured PSP resin and the mechanism(s) of its high char formation, thermal reactions of PSP model compounds were studied.

Although the pyrolysis of styrene and stilbene at over 500°C has been reported,⁴ the pyrolysis of styrylpyridine has not yet been studied. This paper reports the pyrolysis of two styrylpyridines at 200–325°C, the curing temperature range for polystyrylpyridine.

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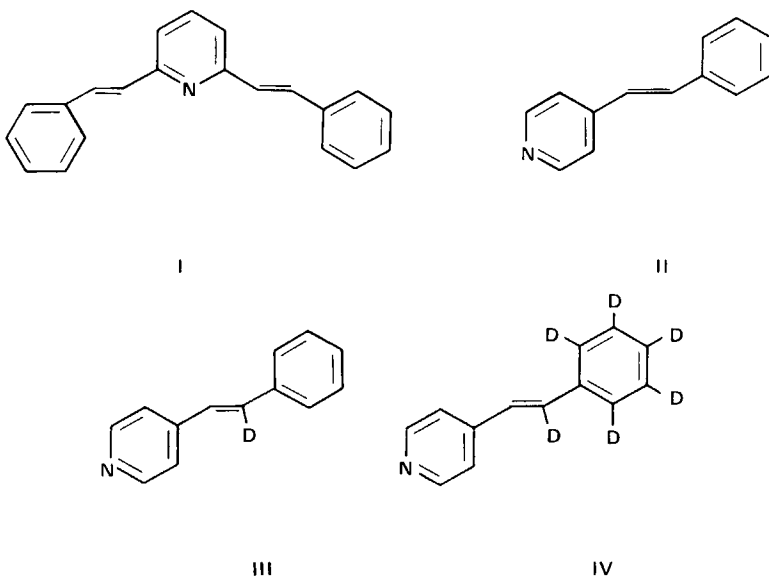
R = CH₃ (COLLIDINE)

R = H (2,6-LUTIDINE)

Fig. 1. Synthesis and curing of polystyrylpyridine.

EXPERIMENTAL

The model compounds used were 2,6-distyrylpyridine (I) and 4-stilbazole (II). Two partially deuterated compounds, 4-stilbazole-*d*₁ (III) and -*d*₆ (IV), were also studied to assist in the identification of the pyrolysis products from 4-stilbazole.



Materials

2,6-Distyrylpyridine (I) was prepared by condensation reaction of 2,6-lutidine and benzaldehyde according to the method of Putney and Soine.⁵ ¹H NMR spectrum (in CDCl₃): 7.4 ppm (multiplet).

ANAL. Calcd for C₂₁H₁₇N: C, 89.05%; H, 6.01%; N, 4.95%. Found: C, 88.74%; H, 6.07%; N, 4.91%.

4-Stilbazole (II) was prepared by reaction of picoline and benzaldehyde in the presence of acetic anhydride.⁶ ¹H NMR spectrum (Fig. 2, in CDCl₃): 8.5 ppm (2H, doublet, J, 6 cps; ortho protons of pyridine ring); 7.3 ppm (8H, multiplet, aromatic protons and olefinic proton next to the phenyl ring); 6.9 ppm (1H, doublet, J, 19 cps, olefinic proton next to pyridine ring). ¹³C NMR spectrum is shown in Figure 3.

ANAL. Calcd for C₁₃H₁₁N: C, 86.19%; H, 6.08%; N, 7.73%. Found: C, 86.23%; H, 6.15%; N, 7.82%.

4-Stilbazole-d₁ (III) was synthesized analogously using benzaldehyde-d₁. ¹H NMR spectrum (in CDCl₃): 8.5 ppm (2H); 7.3 ppm (7H multiplet); 6.9 ppm (1H). ¹³C NMR spectrum is similar to that of 4-stilbazole except that C₅ comprises three small peaks by deuterium coupling.

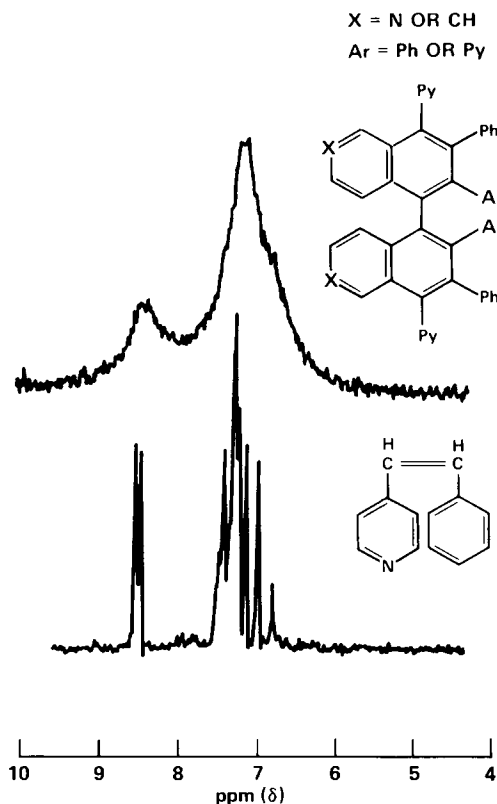


Fig. 2. ¹H NMR spectra of 4-stilbazole and of its polymeric material derivative.

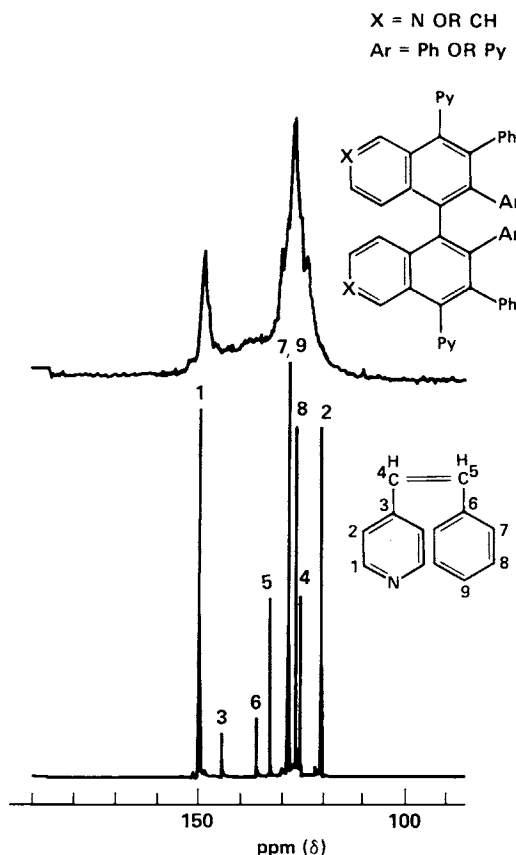


Fig. 3. ^{13}C NMR spectra of 4-stilbazole and of its polymeric material derivative.

ANAL. Calcd for $\text{C}_{13}\text{H}_{10}\text{DN}$: C, 85.71%; H(D), 6.59%; N, 7.69%. Found: C, 85.69%; H(D), 6.61%; N, 7.73%.

4-Stilbazole- d_6 (IV) was synthesized analogously using benzaldehyde- d_6 : mp 128–129°C, yield 40%. ^1H NMR spectrum (in CDCl_3): 8.5 ppm (2H), 7.3 ppm (2H), 6.9 ppm (1H). ^{13}C NMR spectrum: C_1 , 150 ppm; C_2 , 121 ppm; C_3 , 144.5 ppm; C_4 , 126 ppm.

ANAL. Calcd for $\text{C}_{13}\text{H}_5\text{D}_6\text{N}$: C, 83.4%; H(D), 9.1%; N, 7.5%. Found: C, 83.5%; H(D), 9.1%; N, 7.5%.

Analytical Techniques

A DuPont Model 951 thermogravimetric analyzer (TGA) was used for thermal degradation and char yield measurements.

A Varian EM-390 and a Varian CFT-20 NMR spectrometer was used for ^1H and ^{13}C NMR measurements, respectively.

A Perkin-Elmer Model 180 IR spectrophotometer was used for IR spectroscopy. Gel permeation chromatography (GPC) was performed on a Waters Model ALC/GPC 202 HPLC with DuPont SE 60-SE 100 column using DMF as the solvent.

A Hewlett-Packard Model 5980 mass spectrometer (MS) equipped with a data acquisition system was coupled with an H-P Model 5710 gas chromatography to provide mass spectra at 70 eV of individual components of the pyrolysis products from model compounds. The GC column used was 2 m \times 2 mm i.d. glass column packed with 3% OV 101 on 80/100 supelcoport. During analysis, the column temperature was held at 60°C for 2 min and programmed at 32°C/min from 60 to 280°C and then maintained at the upper limit for 12 min; helium flowrate was 22 ml/min.

Thermal Reaction Procedure

The model compounds were sealed in small glass tubes in the presence of air, or in vacuum, and heated at 200–330°C in a constant temperature oven for 24 hr. On cooling, the reaction products were analyzed by TGA and GC/MS. One of the thermal reaction mixtures from 4-stilbazole heated at 325°C in vacuum was distilled at 300°C under vacuum (\sim 1-mm Hg) for 10 min to remove the volatile products. The residue was separated by column chromatography through silica gel. A black polymeric material was collected by eluting with 5% methanol and 95% chloroform. The polymeric material was characterized by NMR, IR, MS, and GPC.

RESULTS AND DISCUSSION

The thermogravimetric analysis of thermally treated and untreated 2,6-distyrylpyridine (I) and 4-stilbazole (II) in nitrogen is shown in Figure 4. These model compounds were previously heated in air or in vacuum for 24 hr at 250°C (for I) or at 313°C (for II). They show weight loss beginning at temperatures below those at which the untreated I and II are volatile (300 and 200°C, respectively), and leveling off at 800°C with residual char. Samples heated in air give higher char yields than those heated in vacuum indicating that oxygen promotes "polymerization" of these compounds. Compound I, with two double bonds, apparently "polymerized" to a greater extent than Compound II, with only one

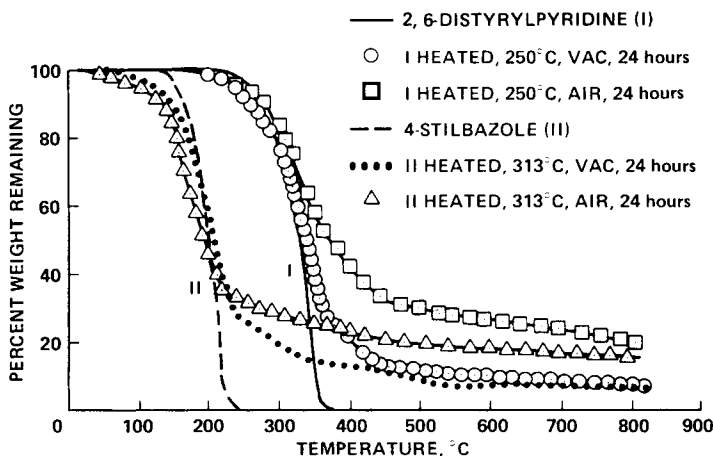


Fig. 4. Thermogravimetric analysis of thermally treated and untreated model compounds in nitrogen with a heating rate of 10°C/min.

double bond. The model compounds were also thermally treated at other temperatures (in the range of 200–325°C) for the same length of time. In general, the sample preheated at higher temperature yields higher char.

The fact that thermally treated samples begin to lose weight at a temperature lower than the corresponding thermally untreated model compounds indicates that the previously heat-treated samples contain other volatile products. Figure 5 shows the gas chromatogram of products from 2,6-distyrylpyridine (I) after being heated in a sealed tube in the presence of air for 25 hr at 200°C. A number of products having molecular weight lower than that of I, as well as its products in which one or both ethylene groups are saturated, were generated during pyrolysis. All GC peaks were identified by MS. Some of the peaks were also identified by comparison to the retention times of known compounds. Mass spectral data and retention times of pyrolysis products from I are shown in Table I. Since 2,6-distyrylpyridine is a relatively large molecule thermally produced dimers could not pass through the GC column. Being a smaller molecule, 4-stilbazole yielded thermal dimeric products which were detected by GC/MS analysis.

Figure 6 shows the chromatogram of pyrolysis products from 4-stilbazole (II) preheated at 325°C for 24 hr in air. The chromatograms of pyrolysis products from deuterated 4-stilbazole III and IV were identical to those of II shown in Figure 6. Disubstituted ethanes as well as stilbene were the major volatile products. Dimeric pyrolysis products of 4-stilbazole were detected at longer retention time. Several small peaks around 10.5–13 min are linear dimers having one or two double bonds but with one phenyl or pyridine group missing. A small peak at 13.2 min is a linear saturated dimer. The major dimer peak at 14.3 min is broad and may contain more than one dimeric structure. The chemical

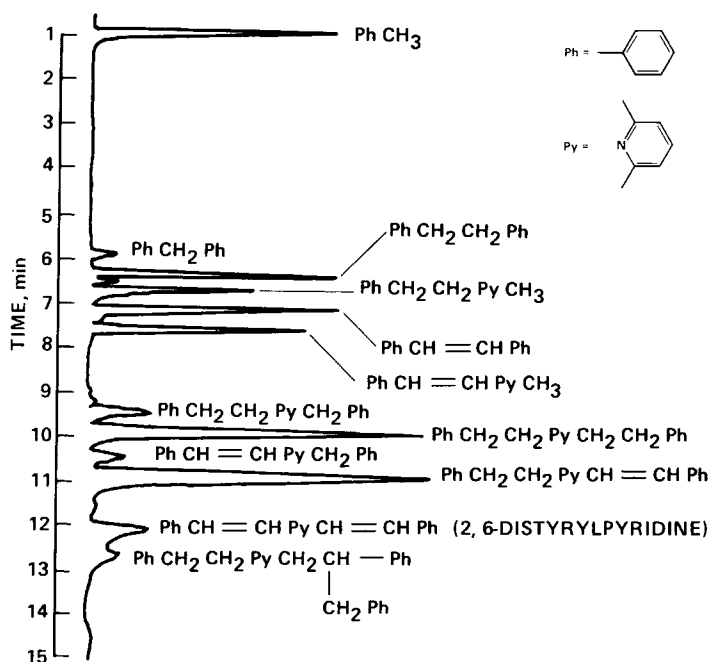


Fig. 5. Gas chromatogram of thermally treated 2,6-distyrylpyridine.

TABLE I
 Mass Spectral Data of Major Pyrolysis Products from 2,6-Distyrylpyridine

Pyrolysis product	GC retention time (min)	m/e (% Relative intensity)
PhCH ₃ ^a	0.9	91(M - 1,100), 92(M,76), 39(20), 65(13), 93(M + 1,5)
PhCH ₂ Ph ^a	5.8	167(M - 1,100), 168(M,90), 165(37), 153(22), 152(21), 91(18), 169(M + 1,12.7)
PhCH ₂ CH ₂ Ph ^a	6.4	91(100), 182(M,16), 65(12), 92(7.5), 183(M + 1,2.4)
PhCH ₂ CH ₂ PyCH ₃	6.7	196(M - 1,100), 197(M,82), 120(M - 77,70), 91(42), 93(37), 198(M + 1,12)
PhCH=CHPh ^a	7.2	180(M,100), 179(M - 1,96), 178(60), 165(40), 181(M + 1,15)
PhCH=CHPyCH ₃	7.6	194(M,100), 195(M + 1,26), 39(8), 84(7)
PhCH ₂ CH ₂ PyCH ₂ Ph	9.5	91(100), 273(M,87), 272(M - 1,78), 196(M - 77,44), 174(M + 1,15)
PhCH ₂ CH ₂ PyCH ₂ CH ₂ Ph	9.9	287(M,100), 91(81), 286(M - 1,76), 210(M - 77,53), 288(M + 1,23)
PhCH=CHPyCH ₂ Ph	10.5	270(M,100), 271(M + 1,36), 91(16), 192(10.9)
PhCH ₂ CH ₂ PyCH=CHPh	10.9	284(M - 1,100), 285(M,95), 91(43), 208(39), 286(M + 1,19)
2,6-Distyrylpyridine (I)	12.1	282(M - 1,100), 283(M,44), 284(M + 1,11), 77(9)
PhCH ₂ CH ₂ PyCH ₂ CHPh CH ₂ Ph	12.7	197(100), 286(M - 91,56), 91(51), 377(M,17), 287(13), 378(M + 1,6.5)

^a The product has the same GC retention time and mass spectrum (Ref. 7) as the authentic sample.

structures assigned for each peak were based on the mass spectrum of that peak and were supported by work with the deuterated samples. Table II shows mass spectral data of major pyrolysis products from 4-stilbazole (II), *-d*₁ (III) and *-d*₆ (IV). After pyrolysis, some olefinic deuterium-hydrogen (D-H) exchange was observed for compounds III and IV, and their pyrolysis products, which were derived from the D-H exchanged starting materials. Aromatic D-H exchange for IV was not observed.

The parent mass peak of the major dimer at 14.3 min (Fig. 6) from the heating of 4-stilbazole is m/e 358, shown in Figure 7. Trisubstituted naphthalene or isoquinoline structures are the most likely structures for this peak. Mass peaks at m/e 280 and 281 are the fragment peaks of trisubstituted isoquinoline or naphthalene with the loss of a phenyl or pyridyl group. A minor linear dimer with one double bond is also present in the broad peak, as indicated by a small m/e parent peak at 362. Mass peaks at m/e 180 and 91 may be fragment peaks of this linear dimer.

The mechanisms proposed for the formation of various major pyrolysis products from 4-stilbazole, including dimers, are shown in Figures 8 and 9. Stilbene was one of the major volatile products, especially when 4-stilbazole was pyrolyzed at a lower temperature (e.g., 282°C). Dipyridylethylene was a minor volatile product, the lower yield of which is probably due to its low thermal stability. Now, it has been reported by Burkle⁸ that stilbazole undergoes photo-dimerization to head-to-tail (H-T) dimer which is not thermally stable; heating the H-T cyclobutane dimer at 260°C for 24 hr yields stilbazole monomer nearly quantitatively. It may be assumed that stilbazole thermally dimerizes to both

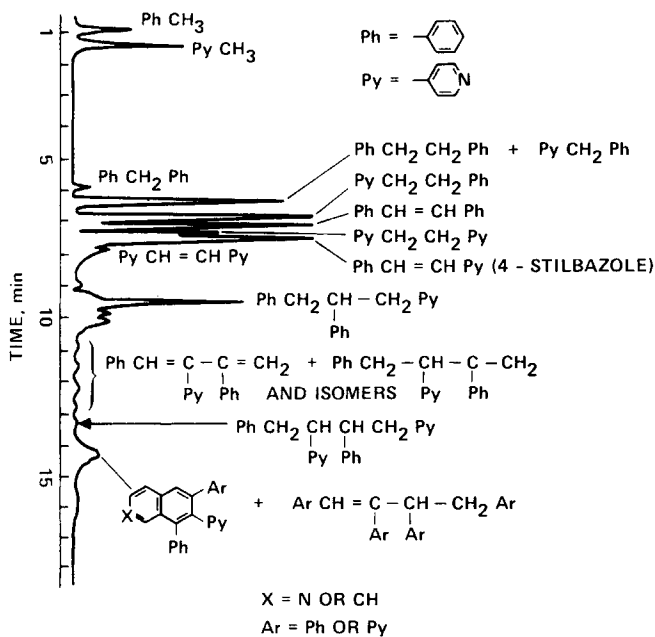


Fig. 6. Gas chromatogram of thermally treated 4-stilbazole.

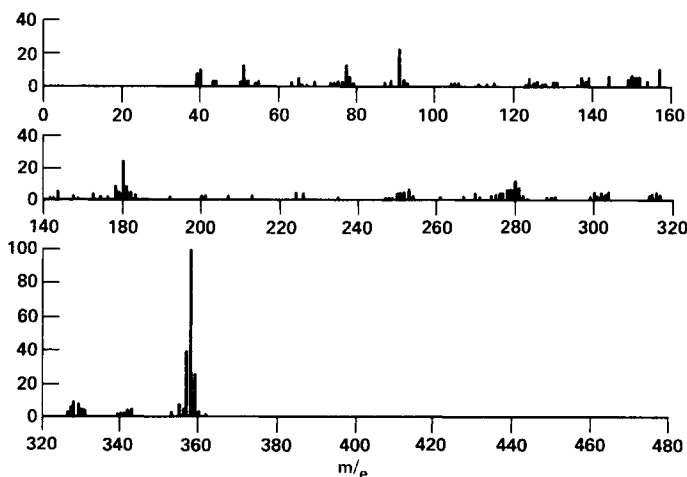


Fig. 7. Mass spectra of 4-stilbazole dimer peak at 14.3 min.

H-T and head-to-head (H-H) cyclobutane dimers. The H-H dimer on thermal dissociation can yield stilbazole (via a) or dipyrindylethylene and stilbene (via b). The cyclobutane dimers that could not be isolated are thus likely intermediates in the thermal reactions of stilbazole.

In this study, we are more interested in the mechanisms for the formation of the thermally stable dimeric or polymeric materials. In the thermal reactions of 4-stilbazole, the formation of isoquinoline or naphthalene type dimer with parent mass peak at m/e 358 may be through the mechanism shown in Figure 9, which is analogous to that for styrene.^{9,10} In the initial thermal reaction of 4-stilbazole, trisubstituted tetrahydronaphthalene, or tetrahydroisoquinoline

TABLE II
Mass Spectral Data of Major Pyrolysis Products from 4-Stilbazole (II), $-d_1$ (III), and $-d_6$ (IV)

Pyrolysis product	GC retention time (min)	m/e (% Relative intensity)
PyCH ₃ ^a	1.4	93(M,100), 66(42), 65(26), 92(M - 1,24)
PyCH ₃ ^b	1.4	93(100), 94(66), 66(51), 67(44), 95(36), 96(6.5)
PyCH ₃ ^c	1.4	94(100), 93(72), 66(65), 95(60), 67(48), 96(20)
PhCH ₂ CH ₂ Ph ^{b,d}	6.4	92(100), 91(50), 93(20), 184(13), 183(10), 185(4.7)
PhCH ₂ CH ₂ Ph ^c	6.4	97(100), 96(50), 98(30), 194(17), 195(7.5), 196(1.4)
PyCH ₂ CH ₂ Ph	6.8	91(100), 183(M,20), 92(7), 184(M + 1,2.8)
PyCH ₂ CH ₂ Ph ^b	6.8	92(100), 91(30), 93(22), 184(20), 185(15), 186(5)
PyCH ₂ CH ₂ Ph ^c	6.8	97(100), 190(33), 96(32), 98(31), 191(17), 192(4.4)
PhCH=CHPh ^{b,d}	7.2	181(100), 180(95), 179(60), 182(52), 183(7)
PhCH=CHPh ^c	7.2	190(100), 191(88), 189(80), 188(70), 192(61), 193(8.7)
PyCH=CHPh (II)	7.5	180(M - 1,100), 181(M,78), 152(21), 153(12), 182(M + 1,12)
PyCH=CHPh (III)	7.5	181(M - 1,100), 182(M,77), 153(26), 154(15), 183(M + 1,12)
PyCH=CHPh ^b	7.5	181(100), 182(81), 153(27), 183(25), 152(18), 154(17)
PyCH=CHPh (IV)	7.5	187(M,100), 185(94), 186(73), 157(22), 188(M + 1,15)
PyCH=CHPh ^c	7.5	186(100), 185(85), 187(82), 188(38), 157(16), 158(13), 189(7.3)
PhCH ₂ CHCH ₂ Py Ph	9.4	182(M - 91,100), 273(M,36), 274(M + 1,7)
PhCH ₂ CHCH ₂ Py ^b Ph	9.4	183(100), 182(58), 184(56), 275(35), 274(21), 276(25), 277(8)
PhCH ₂ CHCH ₂ Py ^c Ph	9.4	188(100), 189(98), 285(54), 286(48), 187(48), 284(35), 287(24)
Major dimers (trisubstituted isoquinoline and naphthalene)	14.3	358(M,100), 357(M - 1,43), 359(M + 1,25), 280(M - 78,19), 281(M - 77,15)
Major dimers ^b	14.3	358(100), 359(69), 360(19), 282(15), 281(13)
Major dimers ^c	14.3	368(100), 369(80), 367(39), 370(20), 290(14), 286(12)

^a Sample has same GC retention time and mass spectrum as the authentic sample.

^b Pyrolysis product derived from III.

^c Pyrolysis product derived from IV.

^d Mass spectrum of unlabeled compound was given in Table I.

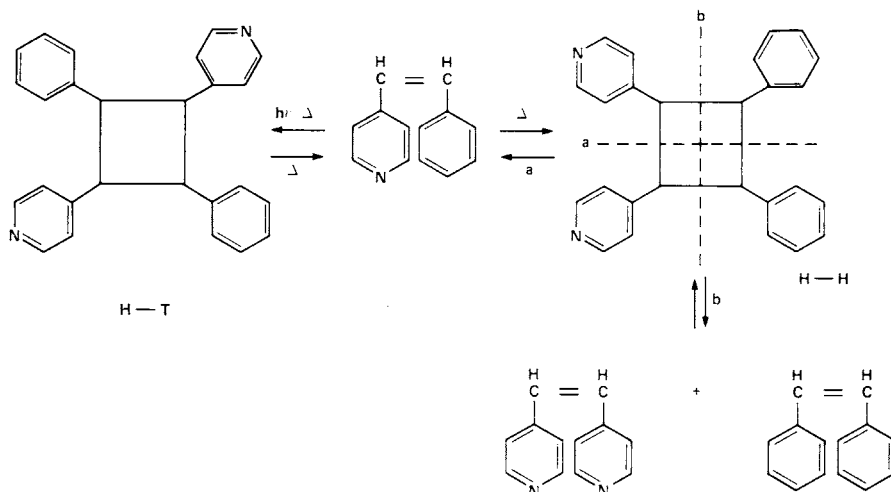


Fig. 8. Mechanism of formation of stilbene and dipyrindylethylene from 4-stilbazole.

is formed by the concerted dimerization (Diels–Alder reaction) of two molecules of stilbazole. This compound is believed to undergo a hydrogen atom transfer reaction with stilbazole to give two radicals (oxygen may promote the free radical formation). The diarylethyl radical may lose a hydrogen or deuterium radical to form starting material. This may account for olefinic D–H exchange of III and IV during pyrolysis. The disubstituted ethyl radical can either abstract a hydrogen or a deuterium atom from another molecule to form disubstituted ethane or react with stilbazole to form dimeric or polymeric materials. Unlike the polymerization of styrene, the disubstituted ethanes were the major volatile products. Linear dimeric materials were the minor products and no linear polymeric materials were isolated. Hence, hydrogen abstraction by disubstituted ethyl radical is a dominant reaction. The substituted tetrahydronaphthalene or tetrahydroisoquinoline radical undergoes hydrogen abstraction to give trisubstituted tetrahydronaphthalene or tetrahydroisoquinoline, which is then dehydrogenated to trisubstituted naphthalene or isoquinoline. The mass spectrum of the major dimer peak at 14.3 min from III showed parent peaks at m/e 358 and 359 for the formation of trisubstituted isoquinoline (M^+ , m/e 358), naphthalene (M^+ , m/e 358) and naphthalene- d_1 (M^+ , m/e 359). The mass spectrum of the major dimer peak at 14.3 min from IV showed parent peak at m/e 368 and 369 for the formation of trisubstituted isoquinoline- d_{10} , naphthalene- d_{10} , and isoquinoline- d_{11} . The high intensity of the m/e 369 peak means the trisubstituted tetrahydroisoquinoline radical undergoes deuterium abstraction from phenyl ring to give trisubstituted tetrahydroisoquinoline, which is then dehydrogenated to trisubstituted isoquinoline- d_{11} . It is possible that two of the tetraline or tetrahydroisoquinoline radicals dimerize to form tetramers, or they react with disubstituted ethyl radical to form trimers.

Any material with a molecular weight higher than the dimer will not pass through the GC column for analysis. The black polymeric material isolated by column chromatography from heated 4-stilbazole (II) may contain tetramers, trimers and/or other polymeric material. The ^1H NMR spectrum of the polymeric material obtained from II is shown in Figure 2 along with that of II itself.

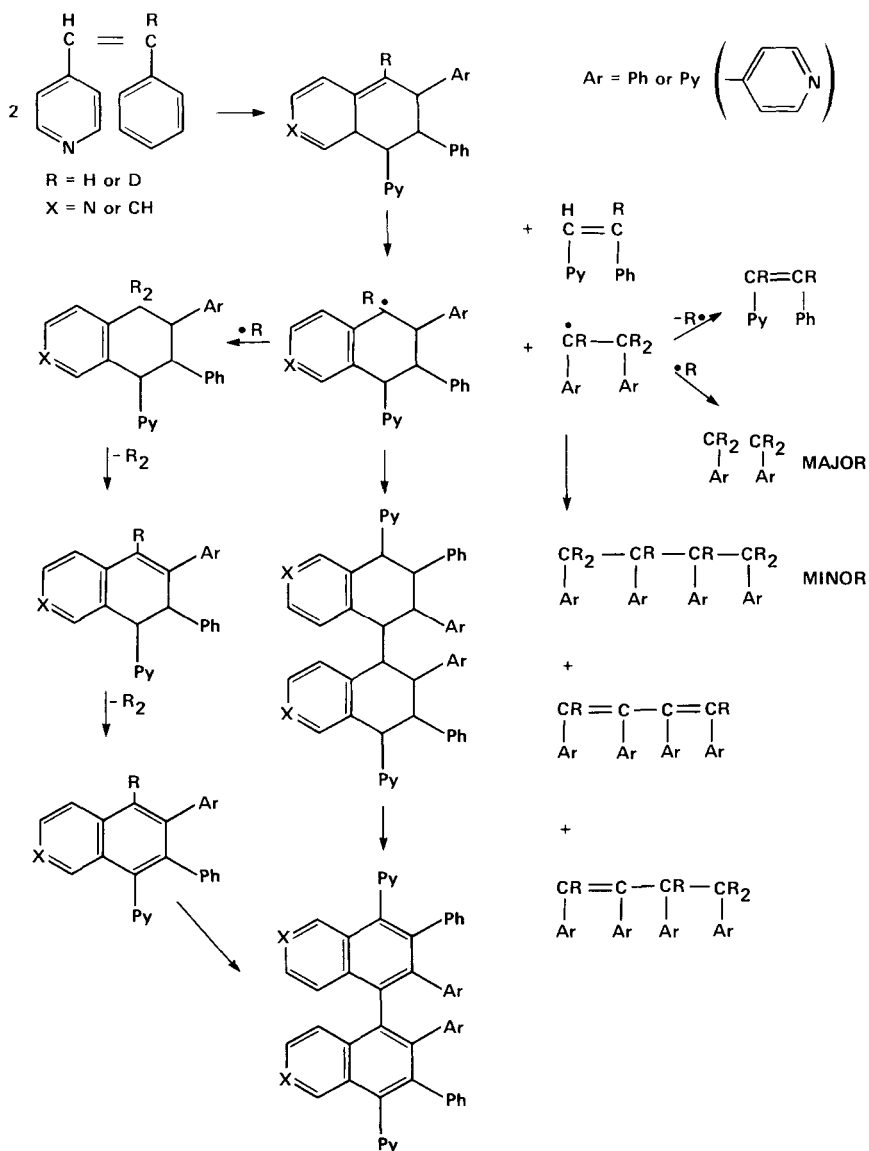


Fig. 9. Mechanism of formation of diarylethane, dimers, and tetramers from 4-stilbazole.

The olefinic protons of 4-stilbazole resonate in the aromatic region and overlap the resonance of the phenyl protons: the two protons ortho to the nitrogen in the pyridine ring are at 8.5 ppm, while the remaining protons are approximately 7 ppm. For the polymeric material only, two broad aromatic proton resonances at 8.5 and 7 ppm were observed. The observed 2:6.4 ratio of these two peaks agrees with the tetramer structure proposed for which a 2:6.5 ratio would be expected. The black polymeric material isolated from heated 4-stilbazole- d_6 (IV) showed a similar 1H NMR spectrum but with a 1:1 ratio of the same two peaks, which would be expected to be in the ratio 1.33:1 for di-isquinoline derivatives and 1:1 for dinaphthalene derivatives.

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