Chemistry of Heterocyclic Compounds. 21. Synthesis of Hexa(2-pyridyl)benzene and the Related Phenyl(2-pyridyl)benzenes. Characterization of Corresponding Substituted Cyclopentenolone Intermediates[1a]

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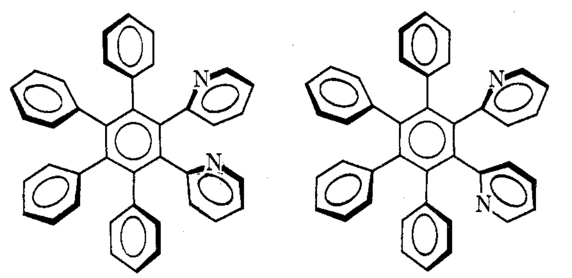
The synthesis and some physical properties of hexa(2-pyridyl)benzene (**41**) and the related phenyl(2-pyridyl)benzenes **30–40** are reported. These compounds were prepared via Diels–Alder reaction of the appropriate acetylene **26–28** with the intermediary dienones **16–25**, which were generated in situ from the corresponding enolones **7–15**. These enolones **7–15** were characterized by analysis of their spectral data.

At the onset of this project, it was hoped that certain stable conformations of poly-2-pyridylbenzenes could be isolated owing to the predicted large barrier to free rotation. Such examples of atropisomerism have not been previously demonstrated. One of the simplest examples is 1,2-di(2-pyridyl)tetraphenylbenzene, which can exist as either β,β



β,β-**31** *β,α*-**31**

or α,β isomer; whereas hexa(2-pyridyl)benzene (**41**) should exist as eight nonsuperimposable conformational isomers including one enantiomeric pair (Figure 1).

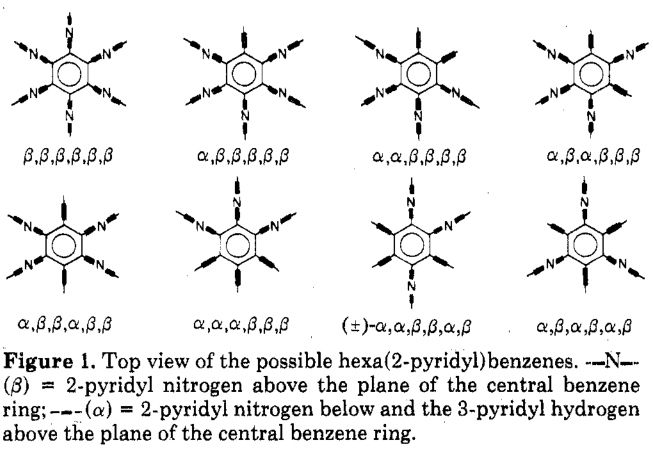


Figure 1. Top view of the possible hexa(2-pyridyl)benzenes. —N— (β) = 2-pyridyl nitrogen above the plane of the central benzene ring; ---(α) = 2-pyridyl nitrogen below and the 3-pyridyl hydrogen above the plane of the central benzene ring.

We herein describe the utilization of the Diels–Alder reaction of cyclopentadienones with the appropriate acetylenes to prepare the previously unknown hexa(2-pyridyl)benzene (**41**) as well as the complete series of related phenyl(2-pyridyl)benzenes (**30–40**) (Figure 2). Although several phenyl(2-pyridyl)cyclopentadienones and cyclopentenolones are known, faulty and/or limited literature data make an accurate interpretation of these known compounds rather tenuous at best. In this paper, we also report the structural assignment of the intermediate substituted cyclopentenolones (**7–15**).

Experimental Section[2]

Substituted Acetones. 2-Pyridylacetonitrile was prepared (80%) from 2-chloromethylpyridine[3] [bp 100–104° (12 mm)] with potassium cyanide in anhydrous dimethyl sulfoxide: bp 79–81° (0.4 mm) [lit.[4] bp 118–120° (13 mm)]; NMR ($CDCl_3$) δ 3.85 ($PyCH_2$–, s, 2 H), 6.95–7.8 (PyH, m, 3 H), 8.45 (6-PyH, d, 1 H); ir (neat) 2220 cm^{-1} (C≡N).

1,3-Di(2-pyridyl)acetone (6) was prepared (60%) from 2-pyridylacetonitrile with 2-picolyllithium in anhydrous ether: bp 115–120° (0.01 mm) [lit.[5] bp 130–135° (0.05 mm)]; mp 80–81° (ether); NMR (CCl_4) δ 3.6 [CH_2 (enol, 60%), s], 3.95 [CH_2CO (keto), s], 5.32 (vinyl H), 6.7–7.7 (PyH, m), 8.1–8.5 (6-PyH, m); ir (CCl_4) 1720 (C=O, w), 1640 (C=H, s), 1460, and 1325 cm^{-1}.

1-Phenyl-3-(2-pyridyl)propan-2-one (5) was synthesized (33%) from phenylacetonitrile with 2-picolyllithium in anhydrous ether: bp 167–173° (3.5 mm) [lit.[6] bp 140–142° (3 mm)]; NMR ($CDCl_3$) δ 3.56 [$PhCH_2$– (enol, 22%), s], 3.79 ($PhCH_2CO$, s), 3.90 ($PyCH_2CO$, s), 5.2 (vinyl H, s), 6.6–7.65 [ArH and –OH (exchanged with D_2O)]; ir (neat) 1720 (C=O), 1650 cm^{-1} (C=COH).

Substituted α-Diketones. Phenyl(2-pyridyl)glyoxal (2) was prepared from *trans*-stilbazole[7] [mp 90–91° (ethanol)] via selenium oxide[8] or concentrated nitric acid[9] oxidation: bp 128–130° (0.2 mm); mp 72–73° (ethanol–petroleum ether, lit.[8] mp 72–72.5°).

2-Pyridil (3) was obtained from commercial sources and recrystallized from absolute ethanol, mp 154–156°.

Substituted Acetylenes. Diphenylacetylene was obtained from commercial sources, mp 59–61°.

Phenyl(2-pyridyl)acetylene was prepared (60% overall) from *trans*-stilbazole via 1-phenyl-2-(2-pyridyl)-1,2-dibromoethane [mp 185–186° (benzene), lit.[7] mp 185–186°], then treated with alcoholic potassium hydroxide: bp 120–122° (0.3 mm) [lit.[7] bp 160–164° (3–4 mm)]; NMR ($CDCl_3$) δ 6.92–7.7 (ArH and PyH, m, 8 H); ir (neat) 2350 cm^{-1} (C≡C).

Di(2-pyridyl)acetylene was prepared from either *trans*-1,2-di(2-pyridyl)ethene[10] or 2-pyridil[11] in greater than 80% yield, mp 69–71° (petroleum ether, lit.[10b] mp 69–70°).

Substituted 4-Hydroxy-2-cyclopenten-1-ones. The following procedure illustrates the general preparation of aryl- and heteroaryl-4-hydroxy-2-cyclopenten-1-ones.

A mixture of 2-pyridil (2.12 g, 0.01 mol), 1,3-di(2-pyridyl)acetone (2.12 g, 0.01 mol), and potassium hydroxide (500 mg) in absolute ethanol (20 ml) was refluxed for 30 min. The mixture was cooled and upon standing crystals formed. Recrystallization from benzene–ethyl acetate afforded a mixture (95:5) of (4*SR*,5*SR*)- and (4*SR*,5*RS*)-4-hydroxy-2,3,4,5-tetra(2-pyridyl)-2-cyclopenten-1-one: mp 147–148°; NMR ($CDCl_3$) δ 4.68 and 4.82 (CO^5CH, 2 s, 1 H), 6.65–7.90 (PyH and –OH, m, 13 H), 8.22–8.70 (6-PyH, m, 4 H); ir ($CHCl_3$) 3350 (–OH), 1700 cm^{-1} (C=O).

All of the substituted 4-hydroxy-2-cyclopenten-1-ones are tabulated with their physical and spectral data in Table I.

Substituted Cyclopentadienones. 2,3,4-Triphenyl-5-(2-pyridyl)cyclopentadienone (19). Enolone **10** (1.05 g, 2.5 mmol) in ethylene glycol (5 ml) was refluxed for 10 min. Upon cooling, trituration with methanol precipitated dark red crystals, which were collected, washed with cold methanol, and recrystallized from methanol, affording (50%) 500 mg of **19**: mp 220–221° (lit.[12] mp 225–226°); NMR ($CDCl_3$) δ 6.8–7.8 (ArH and PyH, m, 18 H), 8.42–8.53 (6-PyH, bd, 1 H); ir (Nujol) 1685 cm^{-1} (C=O); uv–visible (MeOH) 290 nm (ϵ 13100), 241 (13900), 443 (12940).

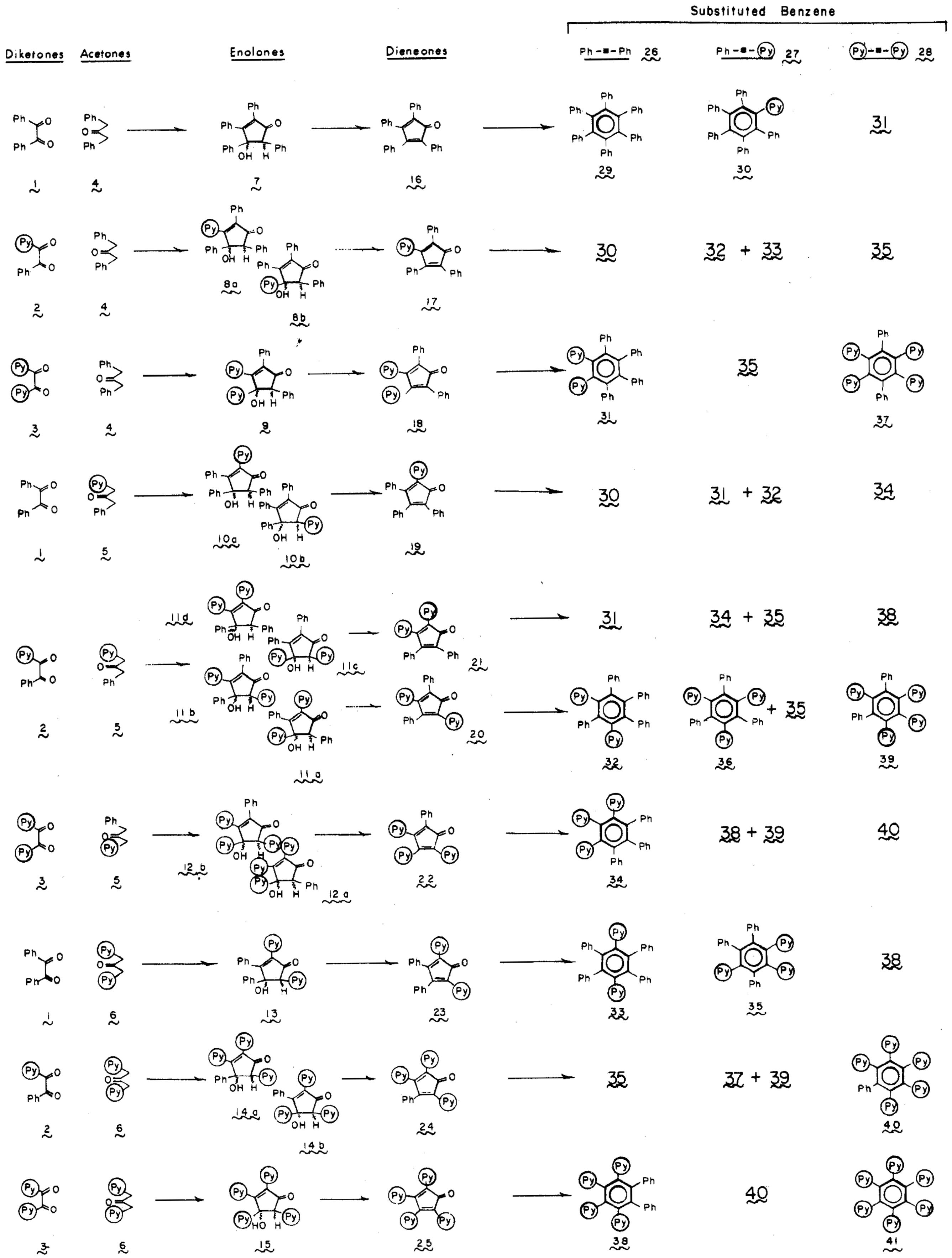


Figure 2.

Anal. Calcd for $C_{28}H_{19}NO$: C, 87.25; H, 4.97; N, 3.64. Found: C, 86.99; H, 4.89; N, 3.60.

2,5-Diphenyl-3,4-(2-pyridyl)cyclopentadienone (18) was prepared (65%) in a similar manner: mp 200–201° (lit.[13] mp 200–201°); NMR ($CDCl_3$) δ 6.50–8.80 (ArH and PyH, m); ir (KBr) 1720 cm^{-1} (C═O); uv-visible (MeOH) 250 nm (ϵ 18950), 493 (643).

Anal. Calcd for $C_{27}H_{18}N_2O$: C, 83.92; H, 4.70; N, 7.25. Found: C, 83.72; H, 4.55; N, 7.20.

Table I
Substituted 4-Hydroxy-2-cyclopenten-1-ones[a]

Starting materials: α-Diketone	Starting materials: Acetone	Enolone product	Substituents 2	Substituents 3	Substituents 4	Substituents 5	Mp, °C (solvent)	Yield,[b] %	Product distribution trans	Product distribution cis	NMR, δ[c] ppm C_5 H	NMR 6-Py H C_2	NMR 6-Py H C_3	NMR 6-Py H C_4	NMR 6-Py H C_5	Ir,[d] cm^{-1} (C=O)
1	4	7[e]	Ph	Ph	Ph	Ph	210 (EtOH)	90	100	0	4.51					1700
2	4	8a[f]	Ph	2-Py	Ph	Ph	139–140 (EtOH)	60	100	0	4.57		8.37			1700
		8b	Ph	Ph	2-Py	Ph		0								
3	4	9[g,h]	Ph	2-Py	2-Py	Ph	188–189 (C_6H_6-EtOH)	80	100	0	4.34		8.28	8.36		1700
1	5	10a	2-Py	Ph	Ph	Ph	147–148 (EtOAc)	83	100	0	4.56	8.60				1630
		10b	Ph	Ph	Ph	2-Py		0								
2	5	11a	2-Py	Ph	2-Py	Ph	148–149 (EtOH)	27	100	0	4.27	8.65		8.40		1700
		11b	Ph	2-Py	Ph	2-Py		3	*i*		4.82		*i*	*i*	*i*	*i*
		11c	Ph	Ph	2-Py	2-Py										
		11d	2-Py	2-Py	Ph	Ph										
3	5	12a	2-Py	2-Py	2-Py	Ph	146–149 (EtOH)	80	90		4.83	8.60	8.28	8.38		1700
		12b	Ph	2-Py	2-Py	2-Py			(10)[i,j]		4.66	*i*	*i*	*i*	*i*	*i*
1	6	13	2-Py	Ph	Ph	2-Py	170–171 (EtOAc)	80	100	0	4.73	8.62			8.49	1660
2	6	14a	2-Py	2-Py	Ph	2-Py	136–137 (EtOH)	70	100	0	4.74	*k*	*k*	*k*	*k*	1725
		14b	2-Py	Ph	2-Py	2-Py										
3	6	15	2-Py	2-Py	2-Py	2-Py	147–148 (EtOH)	80	95		4.68	8.66	8.32	8.42	8.50	1700
										5	4.82	*i*	*i*	*i*	*i*	*i*

[a] Satisfactory analytical data (±0.3% for C, H, N) were reported for all new compounds listed in this table. [b] Reported yields refer to actual isolated crystalline products. [c] 10% w/v, in deuteriochloroform. [d] In chloroform. [e] Lit.[15] mp 208°. [f] Lit.[16] mp 138–140°. [g] Lit.[16] mp 186°. [h] Lit.[13] mp 178–180°. [i] Cannot be determined from limited available data. [j] Either *cis*-12a or *trans*-12b. [k] Broad overlapping multiplet of three hydrogens (δ 8.24–8.69).

Table II
Hexasubstituted Benzenes[a]

Benzene	Starting materials[b]: Enolone (0.01 mol)	Starting materials[b]: Acetylene (mol)	Reaction temp, °C	Yield,[c] %	Mp,[d] °C	Ir,[e] cm^{-1}	Uv,[f] λ, nm (ε × 10^3)	NMR, δ ppm[g] 6-PyH	NMR, δ ppm[g] ArH, PyH
29	7 [16]	26	300	90	465	1450, 1350, 780, 725, 692	247 (59.0)		6.81–7.11
30	7 [16]	27 (0.03)	300	80	466[j]	1580, 1550, 793, 737, 692	247 (52.0)	8.23[h]	6.82–7.15
31	9 [18]	26 (0.025)	350	95	468[k]	1580, 792, 734, 697	246 (62.0)	8.15[h]	6.70–7.46
32	11a, b [20]	26 (0.03)	350	50	476	1590, 790, 745, 695	245 (73.0)	8.21[i]	6.82–7.26
33	13 [23]	26 (0.03)	320	75	474	1600, 790, 740, 695	244 (58.0)	8.22[h]	6.80–7.28
34	12 [22]	26 (0.03)	350	80	473	1580, 784, 731, 695	245 (75.5)	8.20[i]	6.76–7.41
35	13 [23]	27 (0.03)	300	60	470[l]	1595, 1150, 800, 735, 695	246 (58.0)	8.21[h]	6.68–7.18
36	11a, b [20]	27 (0.02)	300	50	479	1570, 1500, 790, 730, 695	245 (62.0)	8.20[i]	6.76–7.43
37	9 [18]	28 (0.02)	300	57	479	1575, 1550, 800, 745, 695	245 (77.5)	8.22[h]	6.74–7.47
38	15 [25]	26 (0.025)	275	75	479	1590, 800, 730, 692	244 (72.5)	8.20[i]	6.76–7.64
39	11a, b [20]	28 (0.025)	300	35	481	1580, 785, 730, 700	244 (60.5)	8.17[i]	6.69–7.43
40	14 [24]	28 (0.03)	250	65	484	1575, 1530, 805, 745, 695	245 (62.0)	8.15[i]	6.62–7.12
41	15 [25]	28 (0.025)	200	70	486	1595, 1150, 810, 755, 720	247 (58.0)	8.16[h]	6.72–7.46

[a] Satisfactory analytical data (±0.3% for C, H, N) were reported for all new compounds listed in the table. [b] Preferred starting materials; however, alternate combinations have been successful; number in brackets in first column designates enone intermediate. [c] Reported yields refer to the actual isolated recrystallized product, from dimethylformamide. [d] DTA values, uncorrected. [e] In Nujol. [f] In 1,2-dichloroethane. [g] Ca. 10% w/v, in dimethylacetamide at 110°, Me_4Si as standard. [h] Observed doublet (J = 2 Hz). [i] Center of the observed two doublets (J = 2 Hz each). [j] Lit.[16] mp 455°. [k] Lit.[16] mp 455°. [l] Lit.[16] mp 468–470°.

Hexasubstituted Benzenes. The following procedure illustrates the general preparation of aryl- and/or heteroarylbenzenes.

A mixture of 4-hydroxy-2,3,4,5-tetra(2-pyridyl)-2-cyclopenten-1-one (4.1 g, 0.01 mol) and di(2-pyridyl)acetylene (4.5 g, 0.025 mol) was heated under nitrogen to 200° for 15 min. After gas evolution and subsequent cooling, the residue was washed with benzene and recrystallized from anhydrous dimethylformamide, affording (70%) analytically pure hexa(2-pyridyl)benzene: mp 486°; NMR (*N,N*-dimethylacetamide, 150°) Figure 3.

All of the aryl- and/or heteroaryl substituted benzenes are tabulated with their physical and spectral data in Table II.

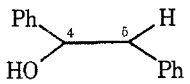
Results and Discussion

Synthesis of Enolones. Classically, cyclopentenolones have been prepared by base-catalyzed condensation of the appropriately substituted 1,3-disubstituted acetones with α-diketones; the general reaction has been reviewed[14] and best exemplified[15] by condensation of **1** with **4** to prepare (90%) tetraphenyl-4-hydroxy-2-cyclopentenone (**7**). 2,5-Diphenyl-3,4-di(2-pyridyl)cyclopentenolone (**9**) was previously synthesized[13,16] from α-pyridil (**3**) and dibenzyl ketone (**4**) in the presence of ethanolic potassium hydroxide at 78°. Although the major isolated reaction product was not structurally assigned, the gross structure of **9** was assigned as based on its thermal conversion to **18**, which also was not isolated but rather trapped by an appropriate dienophile. Similarly, phenyl(2-pyridyl)glyoxal (**2**) was condensed with **4** affording the enolone **8**, whose configuration was assigned to *trans*-**8a** as based on the strong hydrogen bonding exhibited in the ir spectrum of the major isolated product.[16]

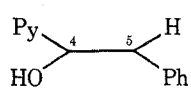
All of the substituted 4-hydroxy-2-cyclopenten-1-ones were prepared in an analogous manner and the physical and spectral data are given in Table I.

Characterization of Enolones. The gross structure proof of the 2-pyridylenolones was established by their thermal dehydration to the corresponding dienones, which were trapped by a symmetrical acetylene such as diphenylacetylene (**26**). Two additional configurational questions need to be clarified: (1) cis or trans C_4–C_5 substituent orientation, and (2) reaction regioselectivity. The structural assignments of **7–15** were determined by NMR spectroscopy coupled with corroborative ir data. In several of the condensation reactions, product mixtures are possible; however, product analysis indicated strong stereoselectivity and regioselectivity. Normally a single isomer was formed either solely or at least predominantly. In the cases where mixtures were formed, the isomers were inseparable. Typical chromatography and recrystallization techniques, which normally would effect separation of such mixtures, were unsuccessful. Presence of the minor isomers was detected by their spectral data.

In addition to the aromatic and hydroxylic hydrogens, the NMR spectrum of **7** exhibited a one-proton singlet at δ 4.51 for the C_5 benzylic hydrogen. Condensation of **2** and **4** afforded a single isolated product, which was assigned *trans*-**8a** as based on the C_5 hydrogen chemical shift (δ 4.57) similarity with **7** suggesting the moiety

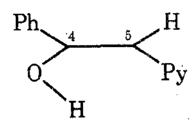


The regioselectivity was established by (1) strong hydrogen bonding (with C_3 pyridyl group) exhibited in the ir spectrum of **8a** and (2) the chemical shift of the C_3 6-pyridyl hydrogen. The benzylic hydrogen is cis to the C_4 phenyl group as indicated by its higher field due to shielding of the aromatic ring;[17] thus, a trans C_4–C_5 diphenyl juxtaposition. Condensation of **1** with **5** afforded *trans*-**10a** as assigned by chemical shift of the C_5 benzylic hydrogen (δ 4.56) and the isolated C_2 6-pyridyl hydrogen (δ 8.60). Dibenzyl ketone (**4**) was condensed with **3** affording a single isolated regioisomer **9**, whose NMR spectrum indicated a single benzylic C_5 hydrogen (δ 4.34) assigned to the moiety



The C_3 6-pyridyl hydrogen chemical shift (δ 8.28) and ir spectral data confirm strong hydrogen bonding (with C_3 pyridyl group).

Condensation of benzil (**1**) and 1,3-di(2-pyridyl)acetone (**6**) gave a single isolated product *trans*-**13**, whose C_5 picolyl hydrogen (δ 4.76) was shifted to lower field indicating the moiety



The strong hydrogen bonding exhibited in the ir spectrum of **13** substantiated the expected cis C_4–C_5 hydroxyl–pyridyl configuration. Reaction of **2** and **6** afforded **14**, whose NMR spectrum confirmed the C_5 picolyl hydrogen (δ 4.74). Since the 6-pyridyl hydrogens exhibited a broad three-proton multiplet, it was impossible to distinguish between structures **14a** and **14b**; however, the probable trans C_4–C_5 phenyl–pyridyl configuration was assigned on steric basis and the hydrogen bonding

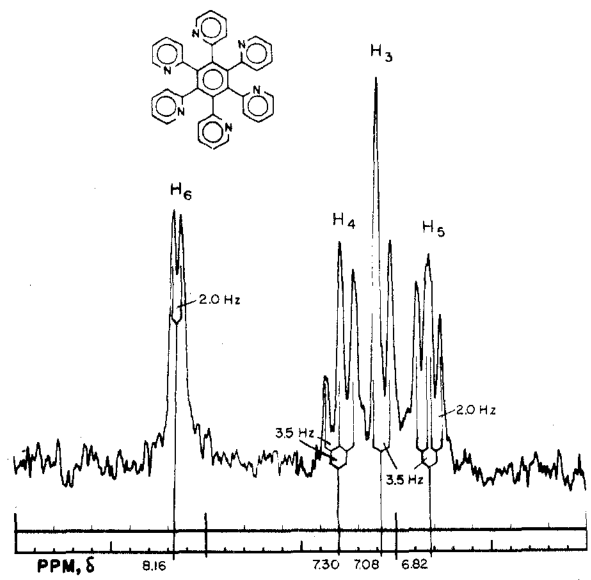
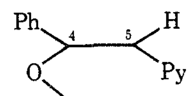
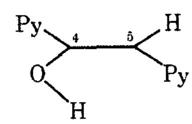


Figure 3. NMR spectrum of hexa(2-pyridyl)benzene in dimethylacetamide at 150°C.



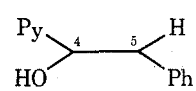
Fortuitously, either **14a** or **14b** affords the single dienone **24**.

Only three condensation reactions afforded inseparable reaction mixtures. Condensation of **3** and **6** generated a mixture of **15** whose isomer distribution cannot arise from regioisomers, thus must be the cis, trans C_4–C_5 substituent geometrical isomers. The NMR spectrum of **15** exhibited the C_5 picolyl hydrogens at δ 4.68 and 4.82 (trans:cis 95:5) whose assignments were based on a greater shielding of the C_5 hydrogen by the C_4 pyridyl group. The second isomeric mixture arose from condensation of **3** and **5** affording **12.** Although two regioisomers are possible, the chemical shift (δ 4.38) of the major isomer is indicative of the moiety



(compare with **9**). The minor (10%) isomer was assigned to either *cis*-**12a** or *trans*-**12b** but, owing to limited data, a distinction cannot be made.

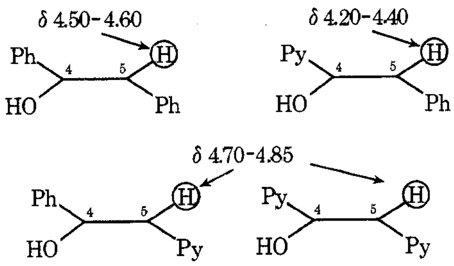
Condensation of **2** and **5** led to a complex mixture of enolones **11**. Pyrolysis of this mixture in the presence of **26** gave predominantly **32,** which was synthesized via an alternate route; thus, the major isomers were **11a** and/or **11b.** The NMR spectrum of **11** exhibited a strong singlet at δ 4.27 indicating the moiety



(compare with **9** or **12a**); thus **11a** is the major isomer. The minor (ca. 3–5%) isomer was assigned either **11b** or **11c** as based on limited spectral data.

Certain generalizations can be drawn from the NMR data of these enolones. (a) Chemical shift data of the C_5 hydrogen singlet, shown in Figure 2, afforded direct evidence to the substituents at C_4 and C_5 on the five-membered ring. (b) The major isolated product preferences under these reaction conditions are shown in Chart I. (c) The chemical

Chart I



shift of the 6-pyridyl hydrogen also depends, albeit to a lesser extent, upon the location of the 2-pyridyl group on the five-membered ring, as shown in Table I.

Synthesis of the Cyclopentadienones. The isolation of pure dienone **16** from enolone **7** is well documented.[15] However, isolation of the 2-pyridyl substituted dienones in an analytical form was the exception rather than the rule. Although the dienones **17–20** and **22–25** were all generated in situ, only **9** and **10a** gave crystalline dienones **18**[18] and **19**,[19] respectively. All other enolones either resisted normal dehydration procedures or, if the desired dienone was generated, it either added water during work-up or was contaminated with starting enolones.

Synthesis of Heteroarylbenzenes. The Diels–Alder condensation[20] of substituted cyclopentadienones (**16–25**), generated in situ from the corresponding tetraaryl- or -heteroarylcyclopentenolones, with acetylenes **26–28** at 200–350° resulted in the formation of the complete series of hexa(2-pyridyl)- and phenyl(2-pyridyl)benzenes. Although the majority of the pyridyl-containing benzenes were readily available from several different combinations, the symmetrical benzene **36** can be synthesized by only one combination of enolone and acetylene. Pyrolysis of cyclopentenolones **11**, consisting of predominantly isomer **11a**, afforded **20** along with the minor isomer **21** (<5% from **11c**). The generation of the preponderant isomer **20** permitted an unambiguous route to **32** and **39** and afforded fortuitously the unique regioisomer **36** when condensed with the unsymmetrical acetylene **27**. The regioselectivity of this Diels–Alder condensation is in agreement with frontier orbital predictions.[21]

All of these hexaaryl–heteroarylbenzenes are colorless, high-melting solids with similar spectral data (Table II). In the uv absorption spectra, all of these compounds have absorption maxima between 245 and 247 nm. The similarity of electronic spectra of pyridylbenzenes **30–41** with hexaphenylbenzene **29** suggest that the steric arrangement of the aryl–heteroaryl substituents are nearly orthogonal to the central benzene ring.[22] The absence of a higher wavelength absorption also indicates the lack of appreciable conjugation. Thus, these heteroarylbenzenes, like hexaphenylbenzene,[22] are semirigid in that the peripheral rings oscillate approximately 10° from orthogonality.

NMR variable temperature studies of these compounds were performed using *N,N*-dimethylacetamide as solvent in the temperature range 70–150°. Owing to the extreme insolubility of these compounds at temperatures below 70°, the NMR spectral data are available only over a limited range. In general, there was no discernible change in the NMR spectral patterns of **30–41** over this limited temperature range.

In summary, the complete series of 2-pyridylbenzenes (**30–41**) has been synthesized in an unambiguous manner from the corresponding characterized cyclopentenolones (**8–15**). From the current spectral and physical data on **31–41**, little useful information can be ascertained concerning their atropisomeric properties. However, from our limited selective complexation studies coupled with high-pressure liquid chromatography, several isomeric mixtures of the less complicated compounds (e.g., **31**) can be detected. Details of these results will be reported later.

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Registry No.—**1**, 134-81-6; **2**, 13474-48-1; **3**, 28348-69-8; **4**, 102-04-5; **5**, 50550-53-3; **6**, 23580-81-6; **7**, 56650-39-6; **8a**, 56650-40-9; **9**, 56650-41-0; **10a**, 56650-42-1; **11** major isomer, 56650-43-2; **11** minor isomer, 56630-16-1; **12** major isomer, 56650-44-3; **12** minor isomer, 56630-17-2; **13**, 56650-45-4; **14a**, 56650-46-5; **14b**, 56650-47-6; (*4SR,5SR*)-**15**, 56679-40-4; (*4SR,5RS*)-**15**, 56679-39-1; **16**, 479-33-4; **17**, 56650-48-7; **18**, 14678-71-8; **19**, 50550-55-5; **20**, 56650-49-8; **21**, 56650-50-1; **22**, 56650-51-2; **23**, 56650-52-3; **24**, 56650-53-4; **25**, 56650-54-5; **26**, 501-65-5; **27**, 13141-42-9; **28**, 28790-65-0; **29**, 992-04-1; **30**, 13867-34-0; **31**, 13698-27-6; **32**, 56650-55-6; **33**, 56650-56-7; **34**, 56650-57-8; **35**, 13698-24-3; **36**, 56679-38-0; **37**, 56679-37-9; **38**, 56650-58-9; **39**, 56650-59-0; **40**, 56650-60-3; **41**, 56679-15-3; 2-pyridylacetonitrile, 2739-97-1; 2-chloromethylpyridine, 4377-33-7; potassium cyanide, 151-50-8; 2-picolyllithium, 1749-29-7; phenylacetonitrile, 140-29-4; *trans*-stilbazole, 538-49-8; *trans*-1,2-di(2-pyridyl)ethene, 13341-40-7.

References and Notes

(1) (a) Previous paper in this series: G. R. Newkome, G. L. McClure, J. Broussard-Simpson, and F. Danesh-Khoshboo, *J. Am. Chem. Soc.*, **97**, 3232 (1975). (b) Based on the Ph.D. Dissertation of N.B.I., Louisiana State University, Baton Rouge, La., 1975. (c) Based in part on the Ph.D. Dissertation of J.M.R., Louisiana State University, Baton Rouge, La., 1973. (d) Grateful acknowledgment is made to the Dr. Charles E. Coates Memorial Fund of the LSU Foundation donated by George H. Coates for the financial aid toward the preparation of these dissertations.

(2) All melting points were taken in capillary tubes with a Thomas-Hoover Unimelt and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Model 621 spectrophotometer and ^{1}H NMR spectra on a Varian Associates HA-100 spectrometer. Tetramethylsilane was used as an internal standard. Microanalyses were performed by Mr. R. Seab in these laboratories. Satisfactory analytical data were obtained on all of the new compounds.

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(18) Dienones **17** and **18** were previously synthesized[16] in situ without isolation.

(19) Dienone **19** was previously synthesized in situ[13] without isolation. Isolation of **19** has been realized;[12] however, their sample was probably contaminated with **16**, since the analytical data are outside the normal deviation.

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