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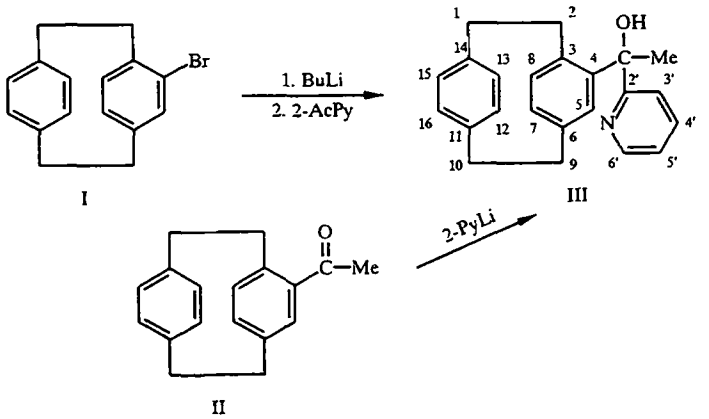
INDOLOPYRIDINES WITH A BRIDGING HETEROATOM. 10.* SYNTHESIS, STRUCTURE, AND ACID CATALYZED REACTIONS OF 1-([2.2]PARACYCLOPHAN-4-YL)-1-(2-PYRIDYL)ETHANOL

L. I. Kryvenko, A. T. Soldatenkov, O. V. Zvolinskii, L. N. Kuleshova, V. N. Khrustalev, V. N. Gryshev, and S. A. Soldatova

Reaction of 2-acetylpyridine with 4-[2.2]paracyclophanyllithium or 4-acetyl[2.2]paracyclophane with 2-pyridllithium gives 1-([2.2]paracyclophan-4-yl)-1-(2-pyridyl)ethanol. Its molecular and crystalline structures have been studied by x-ray analysis. It was found that heating this alcohol in acid medium causes dehydration and heterocyclization to give 1-paracyclophanyl-1-pyridylethylene and 10-methyl[2.2]paracyclophano[4,5-b]indolizine.

A study of the acid catalyzed dehydration of a series of aryl-2-pyridylmethanols [3, 4] has shown that these alcohols are converted in low yield to 5-aryl substituted indolopyridines with a bridging heteroatom. When electron donor groups are introduced into the aryl substituents of similar carbinols the heterocyclization product yield is markedly increased (to 50-95%). In the case of 1-aryl-1-(2-pyridyl)ethanols, dehydration to substituted ethylene is mainly observed [4].

In continuing our work on the synthesis of indolopyridines and [2.2]paracyclophanes it was of interest to study the acid catalyzed reaction of a carbinol containing [2.2]paracyclophanyl, α-pyridyl, and methyl substituents. Hence, reaction of 4-paracyclophanyllithium with 2-acetylpyridine gave 1-([2.2]paracyclophan-4-yl)-1-(2-pyridyl)ethanol (III). The yield of III by this method (benzene, 20-80°C), however, was only 5%.



I III II

*For communication 9 see [1]. This report is also communication [5] in the series "Synthesis, Structure, and Biological Activity of [2.2]Paracyclophanes" (for communication 4 see [2]).

Russian University of National Friendship, Moscow 117198. A. N. Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, Moscow 117813. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 793-800, June, 1997. Original article submitted February 28, 1997.

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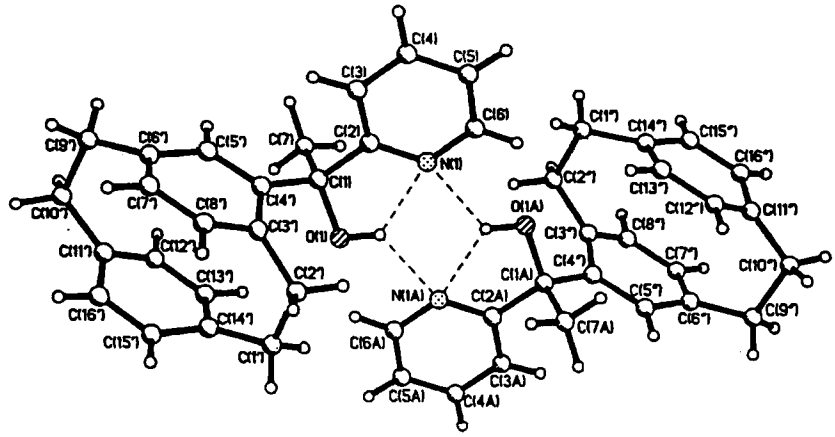


Fig. 1. General view and atom numbering for compound III.

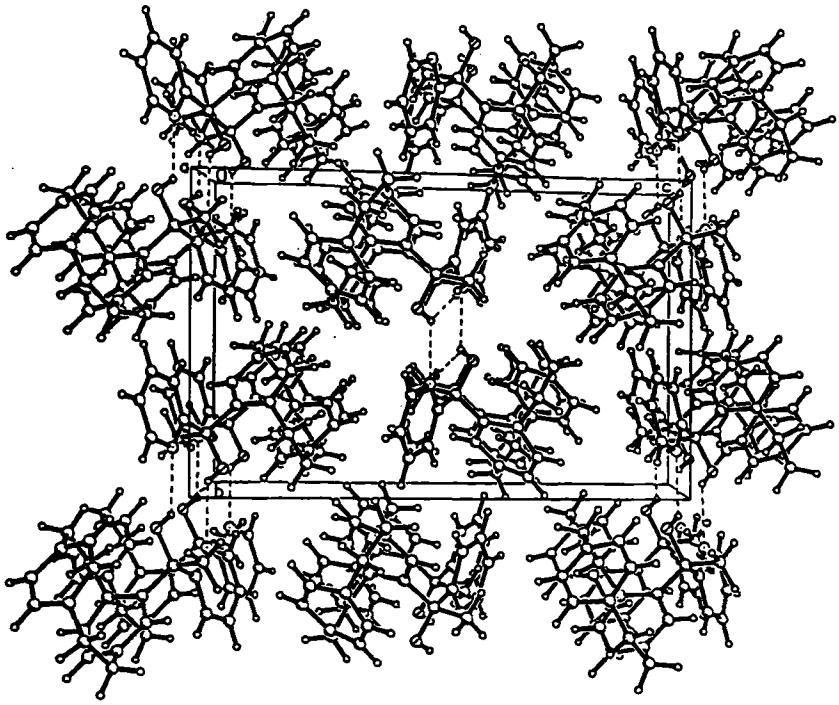


Fig. 2. Packing of the molecule in structure III. Projection along the x axis.

The yield of carbinol III could be increased to 45% using the reaction of 2-pyridyllithium with 4-acetylparacyclophane (II) in absolute alcohol at −70 to −60°C.

The IR spectrum of III, taken as a KBr tablet, showed a broad, associated OH group absorption at 3224-3534 cm^{-1} and a sharp band at 3424 cm^{-1} for the free OH group. The PMR spectrum, recorded in $CDCl_3$, showed a broad singlet for the hydroxyl group at 5.98 ppm, pointing to an intramolecular hydrogen bond. The chemical shifts and multiplicity of the remaining proton signals confirm the carbinol III structure (see Experimental section).

The molecular and crystal structures of III were proved by x-ray analysis. Figure 1 pictures the molecular dimer, achieved in the crystal through H-bonds. Tables 1-4 give the atomic coordinates, bond lengths, and valence angles for molecule III. Overall, the paracyclophane system shows standard values [5-7]. The deviation of the ipso atoms $C_{3'}$, $C_{6'}$, $C_{11'}$, and $C_{14'}$ from the benzene ring averages 12.6° (range of values 12.3-12.9°) as in the unsubstituted paracyclophane, hence this benzene ring assumes a boat conformation. The distance between the bases of the boats is 3.05 Å. The planes of the benzene rings are turned by 2° relative to one another. In contrast to the unsubstituted paracyclophane, where the deviation from the trigonalplanar configuration of the ipso atoms is 11.2°, the ipso atoms in III have a trigonalplanar configuration as

TABLE 1. Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Parameters ($Å^2 \times 10^3$) of Nonhydrogen Atoms in Molecule III

Atom	x	y	z	U_{eq}
$O_{(1)}$	1689(2)	797(1)	9444(1)	62(1)
$N_{(1)}$	-361(2)	1503(1)	10312(1)	48(1)
$C_{(1)}$	2091(2)	1864(1)	9795(1)	42(1)
$C_{(2)}$	668(2)	2298(1)	10153(1)	36(1)
$C_{(3)}$	523(2)	3437(1)	10345(1)	44(1)
$C_{(4)}$	-708(2)	3759(2)	10721(1)	48(1)
$C_{(5)}$	-1771(2)	2938(2)	10888(1)	52(1)
$C_{(6)}$	-1562(2)	1834(2)	10671(1)	57(1)
$C_{(7)}$	3543(3)	1660(2)	10426(1)	61(1)
$C_{(1')}$	1451(2)	953(2)	7783(1)	55(1)
$C_{(2')}$	416(2)	1908(2)	8111(1)	57(1)
$C_{(3')}$	1485(2)	2842(1)	8513(1)	40(1)
$C_{(4')}$	2475(2)	2726(1)	9217(1)	36(1)
$C_{(5')}$	3871(2)	3395(1)	9370(1)	41(1)
$C_{(6')}$	4331(2)	4176(1)	8868(1)	44(1)
$C_{(7')}$	3164(2)	4460(1)	8268(1)	48(1)
$C_{(8')}$	1770(2)	3798(1)	8100(1)	45(1)
$C_{(9')}$	6110(2)	4481(2)	8906(1)	60(1)
$C_{(10')}$	7072(3)	3623(2)	8484(2)	69(1)
$C_{(11')}$	6044(2)	2631(2)	8148(1)	51(1)
$C_{(12')}$	5818(2)	1662(2)	8557(1)	51(1)
$C_{(13')}$	4420(2)	1007(1)	8386(1)	47(1)
$C_{(14')}$	3203(2)	1298(1)	7796(1)	45(1)
$C_{(15')}$	3620(2)	2094(2)	7298(1)	52(1)
$C_{(16')}$	5019(2)	2750(2)	7471(1)	53(1)

TABLE 2. Coordinates ($\times 10^4$) and Isotropic Temperature Parameters ($Å^2 \times 10^3$) for the Hydrogen Atoms in Molecule III

Atom	x	y	z	U
$H_{(1)}$	988(28)	446(21)	9698(13)	101(8)
$H_{(3)}$	1289(21)	3986(16)	10215(9)	54(5)
$H_{(4)}$	-802(20)	4566(16)	10869(9)	53(5)
$H_{(5)}$	-2637(24)	3107(16)	11155(10)	65(5)
$H_{(6)}$	-2289(24)	1221(18)	10787(11)	71(6)
$H_{(7A)}$	3850(26)	2441(21)	10715(12)	85(7)
$H_{(7B)}$	4504(25)	1331(17)	10208(11)	73(6)
$H_{(7C)}$	3204(23)	1111(18)	10738(11)	67(6)
$H_{(1A)}$	1363(22)	247(17)	8076(10)	63(6)
$H_{(1B)}$	880(23)	797(16)	7276(11)	67(6)
$H_{(2A)}$	-275(24)	1508(17)	8422(11)	71(6)
$H_{(2B)}$	-335(25)	2294(17)	7699(11)	69(6)
$H_{(5')}$	4665(21)	3265(15)	9830(10)	52(5)
$H_{(7')}$	3380(22)	5057(16)	7912(10)	64(5)
$H_{(8')}$	1026(21)	3922(14)	7630(10)	51(5)
$H_{(9A)}$	6605(24)	4536(18)	9439(12)	76(6)
$H_{(9B)}$	6218(24)	5249(20)	8704(11)	78(6)
$H_{(10A)}$	7558(30)	4063(21)	8110(13)	99(8)
$H_{(10B)}$	7989(30)	3376(20)	8833(13)	92(8)
$H_{(12')}$	6560(21)	1504(15)	9005(10)	55(5)
$H_{(13')}$	4189(20)	407(15)	8727(9)	50(5)
$H_{(15')}$	2791(22)	2302(15)	6847(10)	55(5)
$H_{(16')}$	5189(23)	3381(18)	7143(11)	72(6)

in the previously described 4-(2-acetylmethylenetetrahydro-4-pyridyl)paracyclophane [8]. One of the dimethylene bridges in III is twisted. The angle $C_{3'}$-C_2-$C_{1'}$-$C_{14'}$ is 12.3° whereas the $C_{6'}$-$C_{9'}$-$C_{10'}$-$C_{11'}$ is 2.3°. The pyridine ring in the molecule

TABLE 3. Bond Lengths (Å) in Molecules III

Bond	Length, Å	Bond	Length, Å
N(1)—C(1)	1,418(2)	C(3')—C(4')	1,418(2)
N(1)—C(2)	1,329(2)	C(4')—C(5')	1,387(2)
N(1)—C(6)	1,344(2)	C(5')—C(6')	1,398(2)
C(1)—C(2)	1,534(2)	C(6')—C(7')	1,379(2)
C(1)—C(4')	1,537(2)	C(6')—C(9')	1,510(3)
C(1)—C(7)	1,542(3)	C(7')—C(8')	1,383(2)
C(2)—C(3)	1,389(2)	C(9')—C(10')	1,569(3)
C(3)—C(4)	1,381(2)	C(10')—C(11')	1,509(3)
C(4)—C(5)	1,374(3)	C(11')—C(16')	1,389(3)
C(5)—C(6)	1,371(3)	C(11')—C(12')	1,391(2)
C(1')—C(14')	1,507(3)	C(12')—C(13')	1,381(2)
C(1')—C(2')	1,590(3)	C(13')—C(14')	1,393(2)
C(2')—C(3')	1,517(2)	C(14')—C(15')	1,391(2)
C(3')—C(8')	1,395(2)	C(15')—C(16')	1,383(3)

TABLE 4. Valence Angles ω (deg) in Molecule III

Angle	ω	Angle	ω
C(2)—N(1)—C(6)	117,8(1)	C(5')—C(4')—C(1)	119,7(1)
O(1)—C(1)—C(2)	110,3(1)	C(3')—C(4')—C(1)	122,6(1)
O(1)—C(1)—C(4')	108,8(1)	C(4')—C(5')—C(6')	123,3(2)
C(2)—C(1)—C(4')	110,3(1)	C(7')—C(6')—C(5')	116,9(2)
O(1)—C(1)—C(7)	107,4(2)	C(7')—C(6')—C(9')	121,8(2)
C(2)—C(1)—C(7)	106,7(1)	C(5')—C(6')—C(9')	120,0(2)
C(4')—C(1)—C(7)	113,2(1)	C(6')—C(7')—C(8')	119,4(2)
N(1)—C(2)—C(3)	121,8(1)	C(7')—C(8')—C(3')	122,7(2)
N(1)—C(2)—C(1)	115,8(1)	C(6')—C(9')—C(10')	113,8(2)
C(3)—C(2)—C(1)	122,2(1)	C(11')—C(10')—C(9')	113,2(2)
C(4)—C(3)—C(2)	119,6(2)	C(16')—C(11')—C(12')	116,6(2)
C(5)—C(4)—C(3)	118,7(2)	C(16')—C(11')—C(10')	120,5(2)
C(6)—C(5)—C(4)	118,3(2)	C(12')—C(11')—C(10')	121,6(2)
N(1)—C(6)—C(5)	123,8(2)	C(13')—C(12')—C(11')	121,0(2)
C(14')—C(1')—C(2')	112,9(1)	C(12')—C(13')—C(14')	120,7(2)
C(3')—C(2')—C(1')	112,4(1)	C(15')—C(14')—C(13')	116,6(2)
C(8')—C(3')—C(4')	116,7(1)	C(15')—C(14')—C(1')	121,2(2)
C(8')—C(3')—C(2')	116,8(2)	C(13')—C(14')—C(1')	121,1(2)
C(4')—C(3')—C(2')	125,1(2)	C(16')—C(15')—C(14')	120,9(2)
C(5')—C(4')—C(3')	117,7(1)	C(15')—C(16')—C(11')	120,8(2)

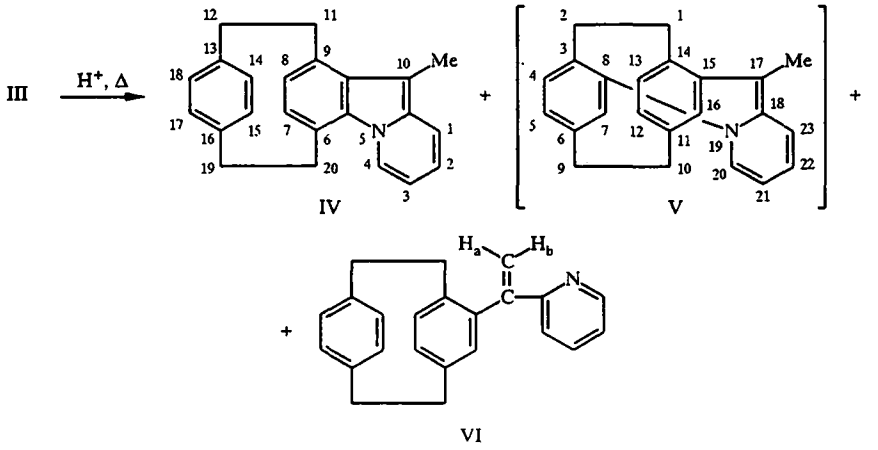
is planar and has usual values [9]. An intramolecular hydrogen bond $O_1-H\cdots N_1$ occurs in the molecule and has the parameters $O_1\cdots N_1$ 2.658 Å, $H\cdots N_1$ 2.12 Å, and $O_1H\cdots N_1$ angle 117°.

The five membered ring formed by the intramolecular hydrogen bond is nonplanar with an $O_1-C_1-C_2-N_1$ torsional angle of 23.1°. The crystalline molecule is associated as a centrosymmetric dimer via intermolecular H-bonds $O_1-H\cdots N_{1A}$ and $O_{1A}-H\cdots N_1$ with the following parameters: $O_1\cdots N_{1A}$ 2.970 Å, $O_1-H\cdots N_{1A}$ 2.34 Å, and $O_1-H\cdots N_{1A}$ angle 127°. The marked deviation of the $O_1-H\cdots N_{1A}$ from linearity is typical for bifurcated (three centered) bonds [10]. In the crystal, the dimers are packed in stacks parallel to the x axis (see Fig. 2). The x-ray data and the melting point range for alcohol III ($\Delta T \simeq 19°C$, see Experimental section) infer that III has liquid crystal properties [11].

Dehydration of alcohol III was carried out over 2 h in refluxing formic acid solution. TLC showed the reaction mixture to be a three component mixture. Chromatography on an alumina column gave four fractions. Fraction 1 (16%) was a 2:1 mixture (PMR data) of polycycles IV and V having identical chromatographic retention. Fraction 2 (16%) was the pure indolopyridine IV and fraction 3 (26%) the disubstituted ethylene VI. Fraction 4 consisted of unreacted alcohol (~33%).

In the PMR spectrum of alkene VI, methyl and hydroxy group signals were absent pointing to dehydration of the starting III. The geminal protons H_a and H_b in the ethylene fragment appeared as two doublet signals at 5.77 and 6.33 ppm respectively with a spin-spin coupling of 1.96 Hz. The marked low field shift for H_b is evidently due to deshielding by the

α-pyridyl substituent which is cis related to it. A similar effect is also seen in relation to one of the protons at C_2 in the paracyclophane fragment. Its multiplet signal is found at 4.25 ppm, i.e., 1.0 ppm to low field when compared to alcohol III.



The PMR spectrum of indolopyridine IV shows two doublet signals at low field from the pyridine fragment (8.34 and 7.46 ppm), the spin-spin coupling of which ($J_{4,3}$ = 7.1 and $J_{1,2}$ = 9.1 Hz) point to formation of the dihydropyridine structure [4]. The CH_3 signal in the pyrrole fragment is seen at 2.65 ppm, i.e., 0.9 ppm to lower field than in the starting alcohol. The aromatic protons of the paracyclophane fragment give four doublet signals (each 1 proton) with a spin-spin coupling of 7.4-7.8 Hz and one broad singlet (J ~ 4.0 Hz) integrating to two proton units assigned to 17-H and 18-H. The 14-H and 15-H protons are seen as an AB type system to high field (at 5.8 and 5.2 ppm, J = 7.8 Hz) due to the shielding effect of the indolizine fragment. Formation of the indolizine fragment in IV is also confirmed by UV spectral data, in which absorption maxima are observed at 408-470 nm, typical of indolizines [3].

The PMR spectrum of fraction 1 includes a series of signals for both compound IV and the polycycle V (the product of transannular heterocyclization) which could not be separated into the pure state. The aromatic proton signal region in the spectrum of IV sharply differs from that of V. In the latter there separate two broad singlet signals at 7.15 and 7.57 ppm ($J_{1/2}$ ~ 2 Hz) which are assigned to benzene protons and point to a transannular cyclization leading to a trisubstituted benzene ring. The remaining four aromatic protons of the paracyclophane fragment occur as a broad signal at 7.17 ppm ($J_{1/2}$ ~ 6 Hz), integrating to a four proton unit. The methyl group signal is 0.13 ppm to higher field than in the case of IV (at 2.52 ppm). The chemical shifts of the dihydropyridine protons of polycycle V also differ slightly from those of IV (see Experimental section). In contrast to that of the pure indolopyridine IV, that of the mixture of IV and V contains additional absorption maxima to shorter wavelength at 265, 272, and 333 nm which can be attributed to polycycle V.

Hence we have, for the first time, brought about the synthesis of an indolopyridine fragment based on a 1-aryl-1-pyridyl substituted ethanol. It was shown that introduction of a paracyclophane substituent into the α-pyridylethanol leads not only to dehydration but also to subsequent electrophilic N−C cyclization. Formation of heterocyclization products in this way points to a significant degree of π-excess in the paracyclophane system.

EXPERIMENTAL

PMR Spectra for the synthesized compounds were recorded on a Bruker AM-200 spectrometer for $CDCl_3$ solutions with TMS as internal standard. IR Spectra were measured on a Specord IR-75 for KBr tablets and UV spectra on a UV-vis spectrophotometer for ethanol solutions. Mass spectra were taken on an MX-1303 instrument with an electron ionization energy of 70 eV. The reaction course and purity of products were monitored using TLC on Silufol UV-254 plates and a hexane-ethyl acetate (3:1) solvent system.

X-Ray Structural Analysis of III. Crystals of III were monoclinic with space group $P2_1/c$. At 20°C a = 8.304(1), b = 11.694(2), c = 18.402(3) Å, β = 99.88(1)°, V = 1760.5(5) Å^3, Z = 4, d_{calc} = 1.243 g/cm^3. Unit cell parameters and the intensities of 3757 reflections were measured on a Siemens P3/PC automatic four circle diffractometer (T 20°C, λMoK α-irradiation, graphite monochromator, $\theta/2\theta$ scanning, θ_{max} = 27°). The structure was solved by a direct method and refined

by a full matrix least squares analysis in the anisotropic approximation for nonhydrogen atoms. Hydrogen atoms (localized directly by Fourier difference synthesis) were refined in the isotropic approximation. The final difference factors were R_1 = 0.043 for 2550 independent reflections with $I > 2\sigma$ (I) and wR_2 = 0.109 for all 3468 independent reflections. All calculations were carried out on an IBM AT-486 PC using the SHELXTLPLUS and SHELXTL-93 programs [12].

1-([2.2]Paracyclophan-4-yl)-1-(2-pyridyl)ethanol (III). A. A solution of 2-acetylpyridine (1.56 ml, 14 mmole) in benzene (5 ml) was added dropwise to a benzene solution of 4-[2.2]paracyclophanyllithium prepared from n-butyllithium (17 mmole) and 4-bromo[2.2]paracyclophane (4 g, 14 mmole) [13] and the product was stirred and heated for 6 h. After cooling, the reaction mixture was treated with a saturated solution of ammonium chloride. The organic layer was separated and the aqueous layer extracted with ether (3 × 50 ml). The combined extracts were dried over $MgSO_4$. Ether was evaporated off and the product was separated chromatographically on an alumina column (h = 30 cm, d = 2 cm, eluent hexane-ethyl acetate 30:1) to give III as colorless crystals (0.23 g, 5%).

B. 4-Acetyl[2.2]paracyclophane (5 g, 20 mmole) was added at −80°C to a solution of 2-pyridyllithium in absolute ether (40 ml), prepared from n-butyllithium (40 mmole) and 2-bromopyridine (2 ml, 20 mmole) [14], and the product was stirred for 1 h at −40 to −30°C. Alcohol III was separated similarly to method A in 0.9 g (45%) yield with mp 124-163°C and R_f 0.61. Found, %: N 4.3. $C_{23}H_{23}NO$. M^+ 329. Calculated, %: N 4.26. M 329. IR Spectrum: 3224-3534 ($OH_{assoc.}$), 3424 cm^{-1} (OH_{free}). UV Spectrum, λ_{max}: 217 (sh), 228, 256, 265, 272 (sh) nm. Mass spectrum, m/z (%): M^+ 329 (33), $[M\text{-}C_5H_5N]^{+\cdot} = \Phi_1$, 250 (47), 236 (53), $[\Phi_1 - OH]^{+\cdot}$, 234 (40), $[M\text{-}104]^{+\cdot}$, 225 (47). PMR Spectrum: 8.52 (1H, d.d., J = 4.8 and 1.1 Hz, 6′ −H); 7.42 (1H, d.d.d, J = 7.8 and 1.7 Hz, 4′ −H); 7.13 (1H, m, 5′ −H), 7.02 (1H, d.d, J = 7.8 and 1.5 Hz, 3′ −H); 6.85 (1H, d, J = 1.5 Hz, 5-H); 6.6-6.4 (5H, m, H_{arom}); 6.27 (1H, d, J = 7.6 Hz, 8-H); 5.98 (1H, br.s, OH); 3.25 and 3.0 (3H and 4H, both m, CH_2); 2.45 (1H, m, 2-H); 1.75 ppm (3H, s, CH_3). ^{13}C Spectrum: 147.5 (2′ −C), 146.1 (6′ −C), 140.6, 140.2, 140.1, 139.2, 139.0 ($C_{quat.}$, paracyclophane), 136.9, 136.7, 134.2, 132.7, 132.6, 132.1, 131.9, 130.4 ($CH_{paracyclophane}$), 120.9 and 121.7 (3′ −C and 5′ −C), 74.3 (C−O), 35.8-35.1 (CH_2), 31.1 ppm (CH_3).

Dehydration and Cyclization of Carbinol III. A solution of III (0.3 g, 1 mmole) in formic acid (10 ml) was refluxed with a reflux condenser for 2 h. The mixture was cooled, poured into water (50 ml), and basified with NaOH solution to pH 10. It was extracted with ether (3 × 30 ml) and dried over $MgSO_4$. The ether was evaporated and the residue chromatographed on an alumina column (h = 30 cm, d = 1.5 cm). Four fractions were separated.

Fraction 1 (eluent hexane) gave 30 mg of a mixture of IV and V (16% based on unreacted alcohol) as a bright yellow oil with R_f 0.69. The UV spectrum of the mixture had absorptions at 218, 238, 265, 272, 293, 333, 345, 359, 402, 423, 455, and 480 nm. PMR Spectrum of V (as a mixture with IV in the ratio 1:2): 8.22 (1H, d, J = 7.1 Hz, 20-H); 7.78 (1H, d, J = 9.1 Hz, 23-H); 7.57 (1H, br.s, 7-H); 7.17 (4H, br.s, 4−, 5−, 12−, and 13-H); 7.15 (1H, br.s, 16-H); 2.52 ppm (3H, s, CH_3). The signals of the remaining protons were obscured by those of IV.

Fraction 2 (eluent hexane) gave indolopyridine IV (30 mg, 16%) as bright yellow crystals with mp 132-135°C and R_f = 0.69. Found, %: N 4.37. M^+ 311. $C_{23}H_{21}N$. Calculated, % N 4.5, M 311. UV Spectrum, λ_{max}: 218, 238, 290 (sh), 300, 345, 361, 408, 428, 455, 470 nm. Mass spectrum, m/z (%): M^+ 311 (50), $[M\text{-}104]^{+\cdot}$, 207 (100). PMR Spectrum: 8.34 (1H, d, J = 7.1 Hz, 4-H); 7.46 (1H, d, J = 9.1 Hz, 1-H); 6.82 (1H, d.d, J = 9.1 and 6.4 Hz, 2-H); 6.5 and 6.62 (each 1H, 2d, J = 7.4 Hz, 7-H and 8-H); 6.45 (1H, t, J = 7.1 and 6.4 Hz, 3-H); 6.37 (2H, br.s, 17-H and 18-H); 5.8 and 5.24 (each 1H, 2d, J = 7.8 Hz, 14-H and 15-H); 3.85 (2H, m, 20-H); 2.95-3.3 (4H, m, 12-H and 19-H); 2.75 (2H, m, 11-H); 2.65 ppm (3H, s, CH_3).

Fraction 3 (eluent hexane−ethyl acetate, 50:1) gave alkene VI as white crystals with mp 151-153°C and R_f 0.37. Found, %: N 4.4. M^+ 311. $C_{23}H_{21}N$. Calculated, %: N 4.5. M 311. UV Spectrum. λ_{max}: 222, 278 nm. Mass spectrum, m/z (%): M^+ 311 (100), $[M\text{-}104]^{+\cdot}$, 207 (50). PMR Spectrum: 8.64 (1H, br.d, J = 4.7 Hz, 6′ −H); 7.5 (1H, d.d.d, J = 7.7 and 1.8 Hz, 4′ −H); 7.18 (1H, m, 5′ −H); 7.0 (1H, d, J = 7.5 Hz, 8-H); 6.89 (1H, d.d, J = 6.5 and 1.5 Hz, 3′ −H); 6.65-6.5 (4H, m, H_{arom}); 6.48 (1H, s, 5-H); 6.45 (1H, d, J = 7.7 Hz, 7-H); 6.33 (1H, d, J = 1.96 Hz, H_b); 5.77 (1H, d, J = 1.96 Hz, H_a); 3.25-2.5 ppm (8H, m, CH_2).

Fraction 4 (eluent hexane−ethyl acetate, 30:1) contained 100 mg (~33%) of starting alcohol III.

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