Carius tube, was heated to 200 °C for 15 h. The crude product was chromatographed on Florisil, and the fraction eluted with methylene chloride–THF (95:5) was crystallized from acetonitrile to give 0.72 g (35%) of **31**: mp 222–225 °C dec; NMR τ 2.3–3.2 (m, 9), 5.9 (d, J = 2 Hz, 2), 7.0 (s, 3).

Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.73; H, 5.13; N, 10.17.

Registry No. 3a, 72917-84-1; **3b**, 72917-85-2; **4a**, 56990-43-3; **4b**, 56948-79-9; **5a**, 72917-86-3; **5b**, 72917-87-4; **6**, 72917-88-5; **7**, 72917-89-6; **8a**, 72917-90-9; **8b**, 72917-91-0; *cis*-**9b**, 72917-92-1; *trans*-**9b**, 72917-93-2; **10a**, 56948-81-3; **10b**, 72917-27-2; **11**, 72917-94-3; **12**, 72917-25-0; **13a**, 56948-89-1; **13b**, 56948-82-4; **13b**·HCl, 72917-95-4; **13c**, 56948-83-5; **14**, 72917-58-9; **15**, 72917-59-0; **17**, 72917-60-3; **17**·HCl, 72925-76-9; **18**, 72917-61-4; **19**, 72917-62-5; **20**, 72917-63-6; **21**, 72917-64-7; **22**, 72917-65-8; **23**, 72917-66-9; **24** (n = 1), 72917-67-0; **24** (n = 2), 72917-68-1; **25a**, 72917-69-2; **25b**, 72917-70-5; **26**, 72917-71-6; **27**, 72917-72-7; **28**, 72917-73-8; **29**, 72917-74-9; **29** imine, 72917-74-9; **30**, 72917-75-0; **31**, 72917-76-1; 9-anthroyl chloride, 16331-52-5; allylamine, 107-11-9; *N*-allyl-9-anthramide, 72917-77-2; *N*-allyl-*N*-methyl-9-anthramide, 72917-78-3; propargylamine, 2450-71-7; *N*-propargyl-9-anthramide, 56948-77-7; *N*-methylpropargylamine, 35161-71-8; *N*-methyl-*N*-propargyl-9-anthramide, 56948-78-8; 9-anthraceneacetic acid, 6624-23-3; 9-anthraldehyde, 642-31-9; 9-anthracenemethanol, 1468-95-7; 9-(chloromethyl)anthracene, 24463-19-2; 9-anthraceneacetonitrile, 2961-76-4; 9-anthraceneacetyl chloride, 72917-30-7; *N*-propargyl-9-anthraceneacetamide, 72925-85-0; *N*-methyl-*N*-propargyl-9-anthraceneacetamide, 72925-86-1; 3-butynylamine, 14044-63-4; *N*-methyl-*N*-(3-butynyl)-9-anthraceneacetamide, 72925-87-2; 2-vinylpiperidine, 37848-70-7; *N*-allyl-9-anthracenemethanimine, 72925-88-3; trifluoroacetic anhydride, 407-25-0; 10-chloro-9-anthraldehyde, 10527-16-9; *N*-allyl-10-chloro-9-anthracenemethanimine, 72925-89-4; 5-chloro-2-methyl-1,2,3,3a,4,5-hexahydro-5,9b-*o*-benzenobenz[*e*]isoindole, 72925-90-7; *N*-propargyl-9-anthracenemethanimine, 56948-80-2; *N*-(3-butynyl)-9-anthracenemethanimine, 72925-91-8; *N*-(1-cyclopentenylmethyl)-9-anthracenemethanimine, 72925-92-9; 1-cyclopentenylmethanamine, 58714-98-0; 2-methyl-1,3,4,5,6,6a-hexahydro-7*H*-7,11b-*o*-benzenobenz[*e*]cyclopent[*h*]isoindole, 72925-93-0; 2-methyl-1,3,4,5,6,6a-hexahydro-7*H*-7,11b-*o*-benzenobenz[*e*]cyclopent[*h*]isoindole hydrochloride, 72925-94-1; *N*-(1-ethynylcyclohexyl)-9-anthracenemethanimine, 72925-95-2; 1-ethynylcyclohexylamine, 30389-18-5; benzylamine, 100-46-9; *N*-benzyl-9-anthracenemethanimine, 14607-11-5; *N*-benzyl-9-anthracenemethanamine, 57447-07-1; propargyl bromide, 106-96-7; *N*-benzyl-*N*-propargyl-9-anthracenemethanamine, 57447-08-2; *N*-allyl-*N*-propargyl-9-anthracenemethanamine, 72925-96-3; 2-(9-anthryl)pyridine, 20308-96-7; *N*-methylallylamine hydrochloride, 72925-97-4; α-(*N*-methylallylamino)-9-anthraceneacetonitrile, 72925-98-5; 9-anthracenemethyl propargyl ether, 72925-99-6; 9-anthracenemethanethiol, 72898-42-1; (9-anthracenemethyl)thiouronium chloride, 72926-00-2; 9-anthracenemethyl propargyl sulfide, 72926-01-3; methyl *cis*-3-[2-(9-anthryl)ethoxy]acrylate, 72926-02-4; methyl *trans*-3-[2-(9-anthryl)ethoxy]acrylate, 72925-74-7; 9-anthraceneethanol, 54060-73-0; methyl propiolate, 922-67-8; 9-anthroic acid, 723-62-6; propargyl alcohol, 107-19-7; propargyl 9-anthroate, 72925-75-8; 4-bromo-1-butene, 5162-44-7; 5-bromo-1-pentene, 1119-51-3; 9-acridinecarboxylic acid, 5336-90-3; 9-acridinecarbonyl chloride, 66074-67-7.

Intramolecular Diels–Alder Additions. 2. Photochemical and Wagner–Meerwein Rearrangements of 9,12-Bridged Ethenoanthracenes[1,2]

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Received October 16, 1978

The direct photolysis of 9,12-bridged ethenoanthracenes, readily accessible by intramolecular Diels–Alder reaction of suitably 9-substituted anthracenes, gives fused dibenzocyclooctatetraenes of type **2**. Sensitized photolysis produces mixtures of the two isomeric dibenzosemibullvalenes, e.g., **12** and **13**. Acid-catalyzed Wagner–Meerwein rearrangements of benzenobenzisoindoles of types **22** and **25** followed by reduction leads to *trans*- and *cis*-tetrahydromethanodibenzocycloheptapyrroles **27** and **28**.

In the first paper of this series,[2] we reported the synthesis of a wide variety of 9,12-bridged ethenoanthracenes by intramolecular Diels–Alder addition of suitably substituted anthracene derivatives. This paper describes some photochemical and Wagner–Meerwein rearrangements of these versatile intermediates.

Results and Discussion

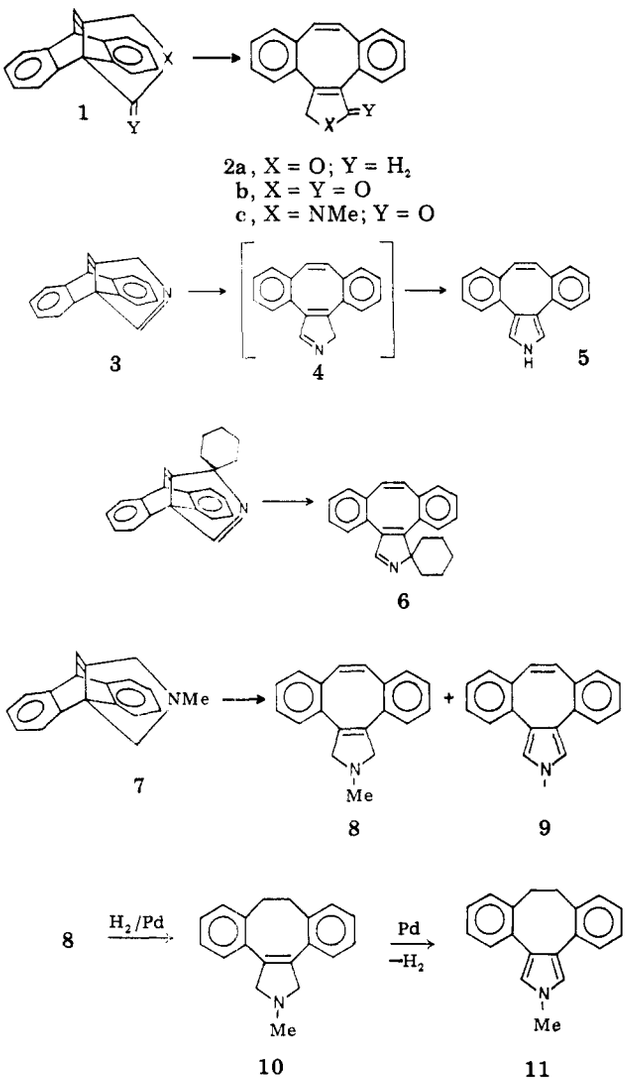
Unsensitized Photolysis. The direct irradiation of ethenoanthracenes gives dibenzocyclooctatetraenes.[3a] Photolysis of 9,12-bridged ethenoanthracenes with unfiltered ultraviolet light in tetrahydrofuran proceeded analogously to give fused dibenzocyclooctatetraenes as shown in Scheme I. Some polymerization always occurred, requiring purification of the photoproducts by chromatography. Yields were in the range of 20–60%. Irradiation of the imine **3** gave 2*H*-dibenzo[3,4:7,8]cycloocta[*c*]pyrrole **5**, presumably by tautomerization of the primary photoproduct **4**. The untautomerized imine could be obtained by blocking the α position with alkyl groups as in the case of **6**. Small amounts of the oxidation product **9** were isolated in the photolysis of the benzenobenzisoindole **7**. The major product, **8**, on catalytic hydrogenation, first took up 1 equiv of hydrogen to give **10** which on further stirring in a hydrogen atmosphere in the presence of a palladium catalyst lost 1 equiv of hydrogen with formation of pyrrole derivative **11**.

Sensitized Photolysis. The acetone-sensitized photolysis of ethenoanthracenes gives dibenzocyclopropapentalenes (dibenzosemibullvalenes).[3b] As in the case of 9-substituted enthenoanthracenes, irradiation of 9,12-bridged ethenoanthracenes in acetone gave mixtures of both possible photoproducts, the composition of which depended on the substitution pattern (Scheme II). The major product from the lactam **1c** was the methenodibenzocycloheptapyrrole **12a** whereas irradiation of the

(1) Some of the compounds described in this paper are claimed in U.S. Patent 4 088 772 (1978).
(2) Paper 1: E. Ciganek, *J. Org. Chem.*, companion paper in this issue.
(3) (a) P. W. Rabideau, J. B. Hamilton, and L. Friedman, *J. Am. Chem. Soc.*, **90**, 4465 (1968); (b) E. Ciganek, *ibid.*, **88**, 2882 (1966).

0022-3263/80/1945-1505$01.00/0

Scheme I

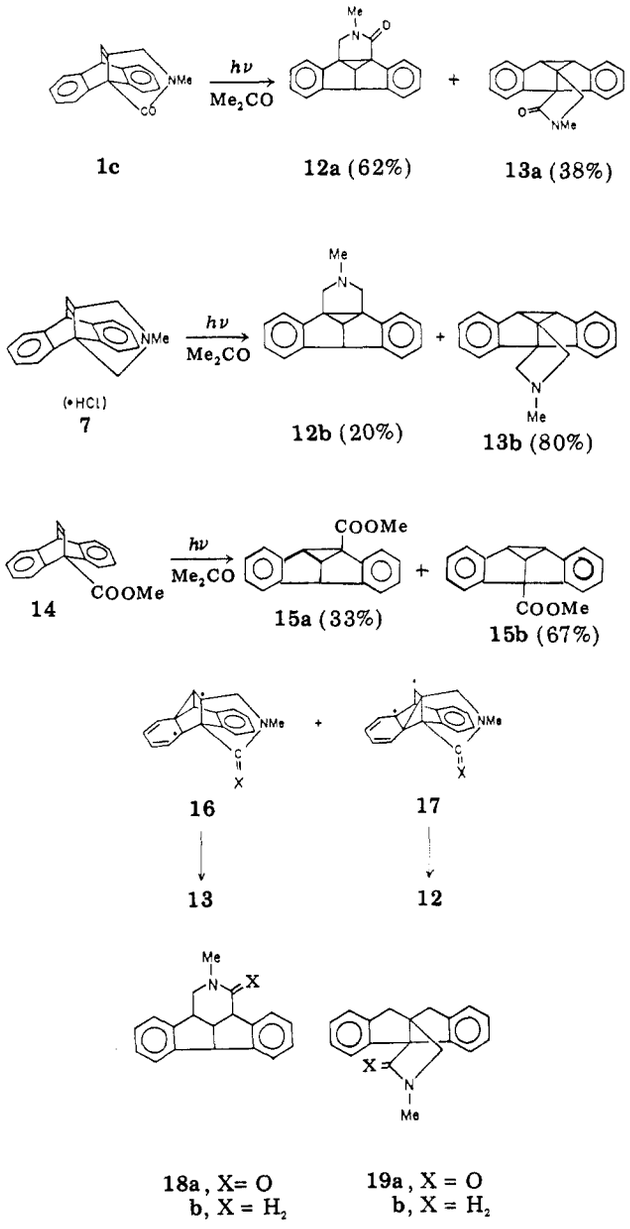


amine **7** (as the hydrochloride) gave predominantly the isomeric 4a,8d-(methaniminomethano)dibenzo[*a*,*f*]cyclopropa[*c*,*d*]pentalene **13b**. Of the two initially formed triplets,[4] the ditertiary diradical **16** should be favored over the tertiary/secondary diradical **17**. This is the case for the photolysis of the amine **7**. Why the situation should be reversed for the lactam **1c** is not immediately clear. By comparison, irradiation of the unbridged ester **14** gave predominantly the photoisomer **15b**.[3b] Destabilization of the cyclopropane ring in the diradical leading to the isomer **15a** by the electronegative ester group has been advanced by Zimmerman et al.[4] as a possible reason for this selectivity.[14] Such an effect cannot operate in the case of lactam **1c**, since it would favor formation of diradical **16** whereas the rearrangement actually proceeds predominantly through diradical **17**.

The amine **12b** was obtained in pure form by reduction of the lactam **12a**. Both **12a** and **13a** underwent hydrogenolysis to give the lactams **18a** and **19a**, respectively. The latter were reduced to the amines **18b** and **19b**.

Wagner–Meerwein Rearrangements. The ethenoanthracene system is very prone to Wagner–Meerwein rearrangement.[5] 9,12-Bridged ethenoanthracenes are no

Scheme II



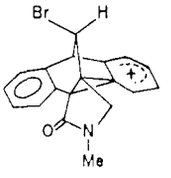
exception. Thus, bromination of the lactam **1c** proceeded rapidly at room temperature with formation of a single dibromide, **20** (Scheme III). The stereochemistry on C-13 follows from $J_{8,13}$ = 4.5 Hz.[6] The orientation of the bromine atom on C-12b is not known, but on mechanistic grounds[7] it is probably on the same side as the methano bridge.[8] The fact that debromination of **20** gave rise to

(4) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973); D. Döpf and H. E. Zimmerman, *Methoden Org. Chem. (Houben-Weyl), 4th Ed.*, **4/5a**, 413 (1975).

(5) S. J. Cristol and M. C. Kochanski, *J. Org. Chem.*, **40**, 2171 (1975), and preceding papers in that series.

(6) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965).

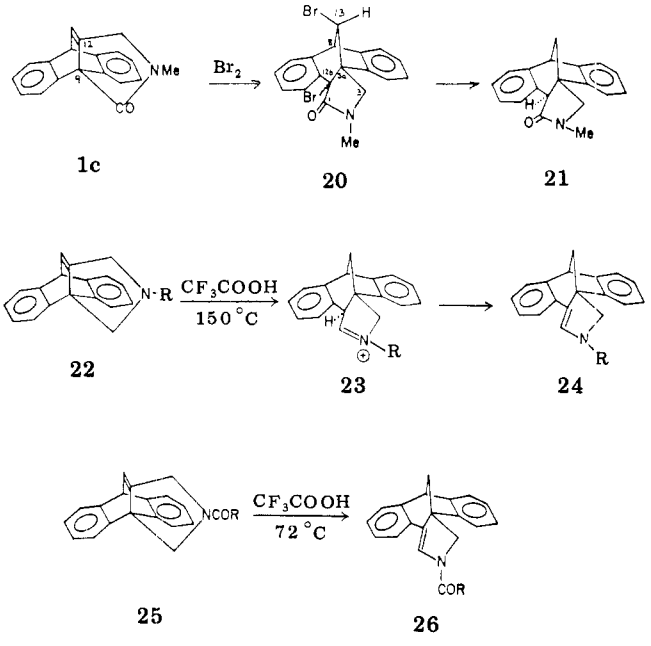
(7) Addition of bromide ion to an intermediate phenonium ion[6] i would result in the proposed stereochemistry.



i

(8) For the purpose of this discussion, the ring system having hydrogen or substituents on C-12b on the same side as the methano bridge is defined as 2,3,8,12-tetrahydro-*cis*-1*H*-3a,8-methanodibenzo[3,4:6,7]-cyclohepta[1,2-*c*]pyrrole.

Scheme III

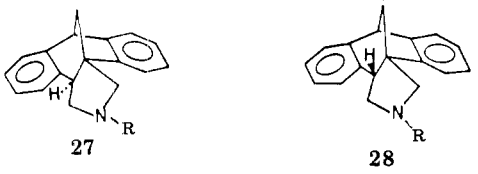


the lactam **21** having the more stable trans stereochemistry[8] as shown is easily explained by inversion on C-12b under the reaction conditions (tributyltin hydride or zinc in dimethylformamide). As in all other Wagner–Meerwein rearrangements in this series, no product derived from initial Br^+ addition to C-12 was detected.

A much more convenient entry into the 1*H*-3a,8-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyrrole system involves acid-catalyzed rearrangements of benzenobenzisoindoles of type **22**. The rearrangement required relatively high temperatures, presumably because protonation occurs first on nitrogen and attack by a proton on the amine salt requires a higher activation energy. Nevertheless, the reaction was very clean when it was carried out in trifluoroacetic acid. Treatment of the intermediate iminium salt **23** with base gave the enamine **24** in high yield. That the salts **23** exist essentially completely in the trans[8] configuration was shown by reduction studies (see below). In this rearrangement, the substituent on nitrogen cannot be hydrogen or a group that is not stable to acid. However, the rearrangement was carried out successfully with the *N*-cyclopropyl derivative.[15]

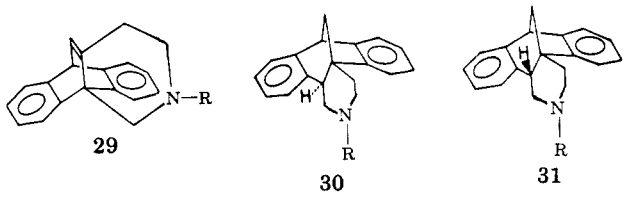
Rearrangement of the amides **25** proceeded at much lower temperatures (72 °C in refluxing trifluoroacetic acid) since protonation of the double bond competes favorably with protonation of the amide. Hydride reduction of the resulting enamides **26** gave the enamines **24**.[16]

Reduction of the enamines **24** with sodium cyanoborohydride in acetic acid/methanol or catalytic hydrogenation in protonic solvents (acetic acid or alcohols) gave the 2,3,8,12b-tetrahydro-*trans*-1*H*-3a,8-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyrroles (**27**); within detectability

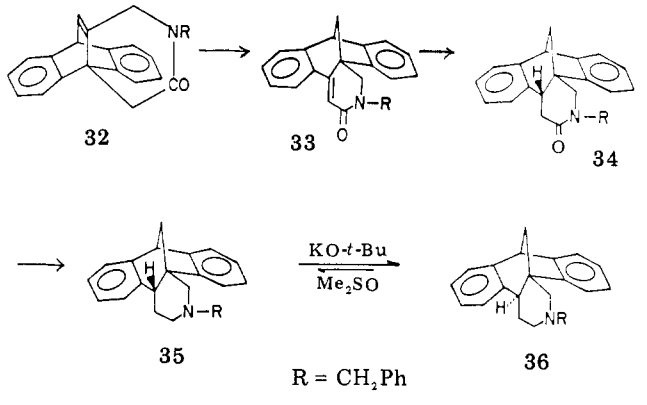


by 220-MHz NMR spectroscopy, the cis isomers **28** were absent. Hydrogenation of the enamines **24** with a palladium catalyst in nonprotonic solvents (tetrahydrofuran, ethyl acetate) gave mixtures of **27** and **28**. By contrast, catalytic hydrogenation of the enamides **26** gave almost exclusively the cis amides (**28**, R = acyl); less than 5% of the trans isomers were usually formed. Hydride reduction of these cis amides provided a convenient route to the cis amines **28** (R = alkyl). As expected, the enamides **26** were not reduced by sodium cyanoborohydride. These results show that in the conversion of the enamines **24** to the trans amines **27**, either by hydride reduction or by catalytic hydrogenation in protonic solvents, the species that is reduced is the iminium salt **23**. It also follows that the salt **23** is considerably more stable than its cis isomer. Base-catalyzed isomerization of the amines **27** and **28** also showed that the equilibrium lies very far on the side of the trans isomers **27**. The stereochemistry of the amine **27** (R = Me) was determined by an X-ray structure determination carried out on its methiodide.[9] The observation that catalytic hydrogenation of the enamides **26** occurred predominantly from above was surprising since models indicate that adsorption to the catalyst should occur equally well from the trans side.

Wagner–Meerwein rearrangements were also carried out with 9,12-bridged ethenoanthracenes having four-membered bridges. Thus, by use of the sequences described above, the amines **29** were converted to the amines **30** (trans) and **31** (cis). The isomeric amines **35** and **36** were



obtained from the lactam **32** as shown. Catalytic hydro-



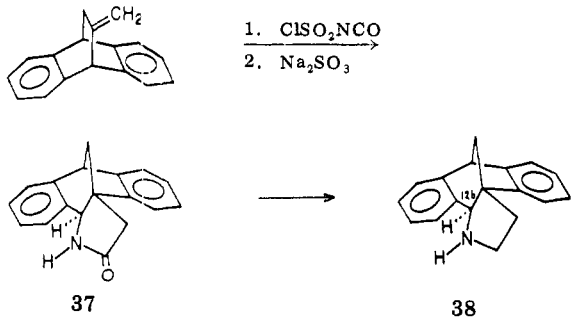
genation of the α,β-unsaturated amide **33** gave predominantly the cis product **34** which on hydride reduction gave the cis amines **35**. Base-catalyzed isomerization of **35** led to an equilibrium mixture containing ca. 75% of **36** and 25% of **35**. The stereochemistry in this series was not rigorously established but rests on an NMR argument (see Experimental Section).

It was of interest to prepare the 1,2,8,12b-tetrahydro-3*H*-3a,8-methanodibenzo[3,4:6,7]cyclohepta[1,2-*b*]pyrroles (**38**), which are isomeric with the amines **27** and **28**. This was accomplished by the reaction of 11-methyleneethanoanthracene with chlorosulfonyl isocyanate in acetonitrile,[10] followed by reduction of the lactam **37**. The

(9) L. Guggenberger, unpublished results.

(10) In ether, the unrearranged β-lactam is formed. We have also investigated the reaction of chlorosulfonyl isocyanate with 9,10-dihydro-9,10-ethenoanthracene in acetonitrile to give 4,5-dihydro-5,1,4-(*o*-benzenometheno)-1*H*-2-benzazepin-3(2*H*)-one. A similar study was since published by another group.[11]

(11) L. A. Paquette and W. C. Volz, *J. Am. Chem. Soc.*, **98**, 2910 (1976).



stereochemistry at C-12b, based on mechanistic arguments, is probably trans[8] as shown.[12]

Experimental Section

Unless noted otherwise, all NMR spectra were determined in $CDCl_3$. **Caution**: benzene is believed to be carcinogenic.

1,3-Dihydrodibenzo[3,4:7,8]cycloocta[*c*]furan (2a). A deoxygenated solution of 1.27 g of 3,5-dihydro-1*H*-5,9b-*o*-benzenonaphtho[1,2-*c*]furan (**1a**)[2] in 100 mL of tetrahydrofuran (THF) was irradiated, under nitrogen, through quartz, with a Philips HPK 125 high-pressure mercury lamp for 9 h. The solvent was removed, and the residue was chromatographed on Florisil. Elution with benzene and crystallization from acetonitrile gave 0.56 g (44%) of **2a**, mp 149–151 °C, which was unchanged on further crystallization: NMR τ 2.6–3.1 (m, 8), 3.3 (s, 2), 4.6–5.3 (symmetrical m, 4).

Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 88.03; H, 5.64.

Dibenzo[3,4:7,8]cycloocta[*c*]furan-1(3*H*)-one (2b). A solution of 1.06 g of 3,5-dihydro-5,9b-*o*-benzenonaphtho[1,2-*c*]furan-1-one (**1b**)[2] in 200 mL of tetrahydrofuran was irradiated in a quartz vessel with a Hanovia 450-W medium-pressure lamp for 3 h. Removal of the solvent and chromatography of the residue on Florisil gave a fraction containing some unreacted starting material (eluted with benzene). Elution with methylene chloride and crystallization from isopropyl alcohol gave 0.31 g (29%) of **2b**, mp 162 °C. An analytical sample had the following: mp 162 °C; NMR τ 2.5–3.0 (m, 8), 3.2 (s, 2), 4.7 and 5.1 (AB q, J = 17 Hz, 2).

Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.15; H, 4.79.

2-Methyl-2*H*-dibenzo[3,4:7,8]cycloocta[*c*]pyrrol-1(3*H*)-one (2c). A solution of 2.03 g of 2-methyl-3,5-dihydro-5,9b-*o*-benzenobenz[*e*]isoindol-1(2*H*)-one (**1c**)[2] in 200 mL of THF was irradiated as above for 8 h. Removal of the solvent and crystallization of the residue from acetonitrile gave 1.03 g (51%) of **2c**, mp 200–203 °C. An analytical sample had the following: mp 201–203 °C; NMR τ 2.6–3.1 (m, 8), 3.1 (s, 2), 5.5–6.3 (AB q, J = 19 Hz, 2), 6.9 (s, 3).

Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.45; H, 5.77; N, 5.13.

2*H*-Dibenzo[3,4:7,8]cycloocta[*c*]pyrrole (5). A deoxygenated solution of 1.00 g of 3,5-dihydro-5,9b-*o*-benzenobenz[*e*]isoindole (**3**)[2] in 150 mL of THF was irradiated, under nitrogen, through quartz, with a Philips HPK 125 high-pressure mercury lamp for 7.5 h. Removal of the solvent and chromatography of the residue on Florisil (elution with benzene) gave 0.6 g of crude product. On crystallization from toluene, 0.22 g (22%) of the pure **5**, mp 191–192 °C, was obtained. An analytical sample had the following: mp 192 °C; NMR τ 1.8 (br, 1), 2.8 (s, 8), 3.2 (s, 2), 3.3 (d, J = 2.5 Hz, 2); UV λ_{max} (cyclohexane) 267 nm (sh, ϵ 5800), 232 (32 500), 218 (36 600).

Anal. Calcd for $C_{18}H_{13}N$: C, 88.86; H, 5.39; N, 5.76. Found: C, 88.89; H, 5.49; N, 5.79.

Spiro[cyclohexane-1,1′-dibenzo[3,4:7,8]cycloocta[1,2-*c*]pyrrole] (6). A solution of 3.0 g of spiro[5*H*-5,9b-*o*-benzenobenz[*e*]isoindole-3,1′-cyclohexane][2] in 200 mL of THF was irradiated as described for **2b** for 3 h. Removal of the solvent gave 3.13 g of a yellow glass which according to NMR spectroscopy contained ca. 50% of **6**: NMR τ 1.9 (s, 1), 2.5–3.2 (m, 8), 3.3 (narrow d, presumably the center signals of an AB q, 2), 7.5–9.0 (m, 10). Reduction of the imine double bond with 2.1 g of sodium cyanoborohydride in methanol (30 mL) and acetic acid (5 mL) overnight gave 3.15 g of a yellow glass. Short-path distillation (175 °C bath, 0.5 μm) of 1.65 g of this product followed by crystallization from acetonitrile gave 0.48 g (30%) of spiro[cyclohexane-1,1′(3*H*)-2*H*-dibenzo[3,4:7,8]cycloocta[1,2-*c*]pyrrole]: mp 147 °C; NMR τ 2.7–3.0 (m, 8), 3.3 (AB q, J = 11 Hz, 2), 6.0 (AB q, J = 14 Hz, 2), 7.9 (s, 1), 7.8–9.5 (m, 10).

Anal. Calcd for $C_{23}H_{23}N$: C, 88.13; H, 7.40; N, 4.47. Found: C, 88.44; H, 7.32; N, 4.53.

2-Methyl-1,3-dihydro-2*H*-dibenzo[3,4:7,8]cycloocta[*c*]pyrrole (8) and 2-Methyl-2*H*-dibenzo[3,4:7,8]cycloocta[*c*]pyrrole (9). A solution of 5.00 g of 2-methyl-1,2,3,5-tetrahydro-5,9b-*o*-benzenobenz[*e*]isoindole (**7**)[2] in 200 mL of tetrahydrofuran was irradiated as above for 3 h. The solvent was removed, and the residue was chromatographed on Florisil. Elution with benzene and crystallization from acetonitrile gave 0.29 g (6%) of **9**: mp 243–244 °C; NMR τ 2.7 (s, 8), 3.1 (s, 2), 3.3 (s, 2), 6.2 (s, 3).

Anal. Calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.56; H, 5.97; N, 5.71.

Crystallization of the fractions eluted with methylene chloride–tetrahydrofuran (1:1) from acetonitrile gave 2.80 g (56%) of **8**. The melting point was erratic; in one determination, the compound melted at 180–182 °C; in another it melted partially at 187 °C and completely at 220 °C. When the compound was cooled and reheated, a melting point of 200 °C was observed. A sample heated to 200 °C for 90 min showed no change in the infrared spectrum: NMR τ 2.8–3.1 (m, 8), 3.3 (s, 2), 5.8–6.4 (m, 4), 7.4 (s, 3).

Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.75; H, 6.59; N, 5.39.

2-Methyl-1,3,8,9-tetrahydro-2*H*-dibenzo[3,4:7,8]cycloocta[*c*]pyrrole (10) and 2-Methyl-8,9-dihydro-2*H*-dibenzo[3,4:7,8]cycloocta[*c*]pyrrole (11). A mixture of 1.97 g of 2-methyl-1,3-dihydro-2*H*-dibenzo[3,4:7,8]cycloocta[*c*]pyrrole (**8**), 100 mL of THF, and 0.5 g of 10% palladium on charcoal was stirred under hydrogen until hydrogen uptake stopped and hydrogen evolution started. The solvent was removed from the filtered solution, and the residue was chromatographed on Florisil. Elution with methylene chloride gave 0.58 g of **11**, mp 138–139 °C, after crystallization from acetonitrile: NMR τ 2.7–3.0 (m, 8), 3.4 (s, 2), 6.4 (s, 3), 6.8 (s, 4).

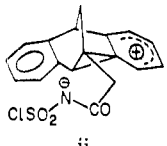
Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.81; H, 6.73; N, 5.44.

The fraction eluted with tetrahydrofuran was dissolved in ether and treated with gaseous hydrogen chloride. The precipitate was crystallized from methanol to give 0.82 g of the hydrochloride of **10**, mp 312–314 °C dec, which was unchanged on further crystallization.

Anal. Calcd for $C_{19}H_{20}ClN$: C, 76.62; H, 6.77; N, 4.70. Found: C, 76.88; H, 6.81; N, 4.91.

The free base has the following NMR spectrum: τ 2.9 (s, 8), 6.0 (s, 4), 6.8 (s, 4), 7.3 (s, 3).

(12) Attack of the nitrogen anion on the phenonium system in the dipole ii would result in the proposed stereochemistry.



ii

(13) S. J. Cristol and J. O. Mayo, *J. Org. Chem.*, **34**, 2363 (1969).

(14) For other recent studies of the selectivity of the di-π-methane rearrangement of ethenoanthracenes and related systems, see: K. E. Richard, R. W. Tillman, and G. J. Wright, *Aust. J. Chem.*, **28**, 1289 (1975); R. G. Paddick, K. E. Richards, and G. J. Wright, *ibid.*, **29**, 1005 (1976); M. Kuzuya, M. Ishikawa, T. Okuda, and H. Hart, *Tetrahedron Lett.*, 523 (1979), and references cited therein.

(15) Experimental details of this rearrangement are given in the Experimental Section for the case of **22** (R = Me); see ref 1 for further examples.

(16) This rearrangement is exemplified in the Experimental Section for the case of **25** (R = cyclopentylmethyl).

2-Methyl-1*H*,8*H*-3a,8,12b-methenodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyrrol-1-one (12a). A deoxygenated solution of 3.18 g of **1c**[2] in 150 mL of acetone was irradiated, under nitrogen, through a Pyrex filter, with a Philips HPK 125 high-pressure mercury lamp for 15 h. The NMR spectrum of the crude product showed the presence of a 62:38 mixture **12a** and 10-methyl-4b,8d-(methaniminomethano)dibenzo[*a*,*f*]cyclopropa[*cd*]pentalen-11-one (**13a**). Crystallization from acetonitrile gave pure **12a**, mp 205–206 °C. An analytical sample had the following: mp 206–206.5 °C; NMR τ 2.1–2.8 (m, 8), 5.3, 6.1 (AB q, J = 6 Hz, 2), 5.7 and 6.1 (AB q, J = 11 Hz, 2), 6.8 (s, 3).

Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.49; H, 5.51; N, 5.02.

10-Methyl-4a,8d-(methaniminomethano)dibenzo[*a*,*f*]-cyclopropa[*cd*]pentalene (13b). A deoxygenated mixture of 3.28 g of **7**,[2] 100 mL of water, 100 mL of acetone, and 5 mL of 10% hydrochloric acid was irradiated, under nitrogen, through a Pyrex filter, with a Philips HPK 125 high-pressure mercury lamp for 30 h. The mixture was concentrated to remove the acetone, made basic, and extracted with methylene chloride to give 3.15 g of an 80:20 mixture of **13b** and 2-methyl-1,2-dihydro-3a,8,12b-methenodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyrrole (**12b**). It was converted to the hydrochlorides with hydrogen chloride in methanol. Crystallization from isopropyl alcohol gave the hydrochloride of **13b**, mp 285 °C dec.

Anal. Calcd for $C_{19}H_{18}ClN$: C, 77.14; H, 6.13; N, 4.73. Found: C, 77.27; H, 6.11; N, 4.85.

A small sample of the pure hydrochloride was reconverted to the free base: NMR τ 2.6–3.1 (m, 8), 6.6–6.9 (three two-proton singlets), 7.5 (s, 3).

2-Methyl-1,2-dihydro-3a,8,12b-methenodibenzo[3,4:6,7]-cyclohepta[1,2-*c*]pyrrole (12b). The mixture of **12a** and **13a**, obtained on sensitized photolysis of 3.2 g of **1c** (see above), was stirred with 50 mL of 1 M diborane in tetrahydrofuran at room temperature overnight and then heated under reflux for 6 h. The excess diborane was destroyed by addition of dilute hydrochloric acid (ice bath), the solvents were removed, and the residue was heated under reflux with a 1:1 mixture of methanol and concentrated hydrochloric acid for 24 h. The solvents were removed, and the residue was made basic and extracted with methylene chloride. Removal of the solvent from the dried extracts gave 2.2 g of a product mixture which was converted to the hydrochloride (2.2 g) with hydrogen chloride in ether. Crystallization from 8 mL of ethanol gave 0.86 g of the hydrochloride of **12b**. It darkened without melting above 250 °C.

Anal. Calcd for $C_{19}H_{18}ClN$: C, 77.14; H, 6.13; N, 4.73. Found: C, 77.36; H, 6.04; N, 4.52.

A small sample of the hydrochloride was reconverted to the free base: NMR τ 2.6–3.0 (m, 8), 5.4 (d, J = 6 Hz, 1), 6.0 (d, J = 6 Hz, 1), 6.4–6.8 (AB q, J = 9 Hz, 4), 7.3 (s, 3).

2-Methyl-2,3,3a,7b,11b,11c-hexahydro-1*H*-dibenzo-[2,3:4,5]pentaleno[1,6-*cd*]pyridine (18b). Hydrogenation of **12a** with palladium on charcoal in THF at room temperature and atmospheric pressure gave 2-methyl-1,7b,11b,11c-tetrahydro-2*H*-dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pyridin-3(3a*H*)-one (**18a**): NMR τ 2.4–3.0 (m, 8), 5.2 (d, J = 7 Hz, split further, 1), 5.8 (d, J = 7 Hz, 1), 6.0–7.5 (m and s, 7).

A mixture of 5.55 g of **18a** and 130 mL of 1 M BH_3·THF was heated under reflux overnight, the excess diborane was decomposed by the slow addition of 30 mL of concentrated hydrochloric acid (ice bath), and the THF was removed under vacuum. Concentrated hydrochloric acid (25 mL) and methanol (25 mL) were added, and the mixture was heated under reflux for 8 h, cooled, made basic, and extracted with methylene chloride. Removal of the solvent from the filtered and dried extracts gave 2.74 g of a semisolid, which on crystallization from 130 mL of acetonitrile gave 1.50 g of **18b**: mp 238–239 °C; NMR (at 220 MHz) τ 2.5–2.7 (m, 2), 2.7–3.0 (m, 6), 5.1 (d, J = 8 Hz, 1), 6.2–6.6 (m, 3), 7.1–7.4 (AB q, J = 12 Hz, split into doublets, J = 4 and 6 Hz, for the low- and high-field components, respectively, 4), 7.8 (s, 3).

Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36. Found: C, 86.97; H, 7.17; N, 5.33.

The compound is quite soluble in benzene but poorly soluble in polar solvents.

12-Methyl-4b,9,9a,10-tetrahydro-4b,9a-(methaniminomethano)indeno[1,2-*a*]indene (19b). Catalytic hydrogenation (Pd/C, THF) of the mother liquors from the crystallization of the mixture of **12a** and **13a** and fractional crystallization of the product from acetonitrile gave **19a**: NMR τ 2.2–2.5 (m, 2), 2.7–3.0 (m, 6), 6.6 (s, 2), 6.9 (s, 4), 7.3 (s, 3).

Diborane reduction of 1.39 g of **19a** as described for **18a** (above) gave 1.34 g of **19b** as an oil that slowly solidified: NMR τ 2.4–3.0 (m, 8), 6.4–7.1 (AB q, J = 16 Hz, 4), 6.9 (s, 2), 7.2 (s, 2), 7.6 (s, 3). The free base was soluble in the conventional organic solvents including hexane. It was converted to the maleate (mp 197–197.5 °C, 1.10 g) with 0.53 g of maleic acid in 2 mL of acetonitrile. An analytical sample had a melting point of 195 °C.

Anal. Calcd for $C_{23}H_{23}NO_4$: C, 73.19; H, 6.14; N, 3.71. Found: C, 73.30; H, 6.08; N, 3.75.

12b,13-Dibromo-2,3-dihydro-2-methyl-3a,8-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyrrol-1(12b*H*)-one (20). To a solution of 0.88 g of **1c**[2] in 10 mL of methylene chloride was added 0.58 g of bromine in 10 mL of methylene chloride. Removal of the solvent left 1.42 g of **20**, mp 215–216 °C dec. An analytical sample (acetonitrile) had the following: mp 221–222 °C dec; NMR τ 1.6–1.8 (m, 1), 2.3–2.8 (m, 7), 5.1 (d, J = 4.5 Hz, 1), 5.7 (d, J = 4.5 Hz, 1), 5.7 (d, J = 10.5 Hz, 1), 5.8 (d, J = 4.5 Hz, 1), 6.6 (d, J = 10.5 Hz, 1), 6.9 (s, 3).

Anal. Calcd for $C_{19}H_{15}Br_2NO$: C, 52.68; H, 3.49; N, 3.24. Found: C, 52.83; H, 3.43; N, 3.34.

2-Methyl-2,3-dihydro-*trans*-3a,8-methanodibenzo-[3,4:6,7]cyclohepta[1,2-*c*]pyrrol-1(12b*H*)-one (21). A mixture of 8.07 g of **20**, 17.2 g of freshly distilled tributyltin hydride, and 50 mL of anhydrous benzene was heated under reflux under nitrogen for 3 days. Most of the benzene was removed, and the residue was short-path distilled (to a 125 °C bath temperature, 1 μm). The pot residue was crystallized from isopropyl alcohol to give 3.63 g (71% yield) of **21**, mp 141–146 °C. An analytical sample, mp 143–143.5 °C, was prepared by sublimation at 170–190 °C (0.5 μm) followed by crystallization from isopropyl alcohol: NMR τ 2.1–2.5 (m, 1), 2.6–3.2 (m, 7), 6.0 (d, J = 10 Hz, 1), 6.1 (dd, J = 4, 2 Hz, 1), 6.8 (d, J = 10 Hz; narrow m, 2), 7.0 (s, 3), 7.6–8.0 (m, 2).

Anal. Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.60; H, 6.57; N, 4.95.

2-Methyl-2,3,8,12b-tetrahydro-*trans*-1*H*-3a,8-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyrrole (27, R = Me) from 21. A mixture of 1.65 g of **21** and 50 mL of 1 M diborane in THF was heated under reflux for 24 h. To the cooled mixture was added slowly 10 mL of concentrated hydrochloric acid, the THF was removed under vacuum, concentrated hydrochloric acid (10 mL) was added to the residue, and the mixture was heated under reflux for 7 h. After concentration to a small volume, the mixture was made basic and extracted with methylene chloride. Removal of the solvent from the dried extracts gave 1.57 g of **27** as an oil: NMR (220 MHz) τ 2.6–3.1 (m, 8), 5.9 (d, J = 4 Hz, 1), 6.0 (d, J = 10 Hz, 1), 6.3 (t, probably dd, 1), 6.6 (dd, J = 8, 10 Hz, 1), 7.0 (d, J = 10 Hz, and additional bands, 2), 7.2 (s, 3), 7.4 (dd, J = 10, 4 Hz, 1), 7.5 (d, J = 10 Hz, 1). It was converted to the hydrochloride which melted at 255–257 °C dec after crystallization from acetonitrile.

Anal. Calcd for $C_{19}H_{20}ClN$: C, 76.62; H, 6.77; N, 4.70. Found: C, 76.77; H, 6.56; N, 4.70.

2-Methyl-2,3-dihydro-8*H*-3a,8-methanodibenzo[3,4:6,7]-cyclohepta[1,2-*c*]pyrrole (24, R = Me) from 22. A mixture of 20 g of **22** (R = Me)[2] and 80 mL of trifluoroacetic acid, contained in an evacuated, sealed Carius tube, was heated to 150 °C for 8 h. The solvent was removed, the residue was dissolved in methylene chloride, and the cooled solution was made basic with 15% aqueous sodium hydroxide solution. Removal of the solvent from the dried methylene chloride solution gave 19.6 g of essentially pure **24** (R = Me). A sample was crystallized from isopropyl alcohol: mp 119.5–120 °C; NMR τ 2.5–3.3 (m, 8), 3.9 (s, 1), 6.1 (d, J = 10 Hz, 1), 7.3 (s, 3), 7.4–7.9 (AB q, J = 9 Hz, the lower field component is split again by 4 Hz and the high-field component by ca. 1 Hz, 2); UV λ_{max} (cyclohexane) 337 nm (ϵ 9000).

Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.66; H, 6.74; N, 5.45.

2-(Cyclopentanecarbonyl)-2,3-dihydro-8*H*-3a,8-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyrrole (26, R = Cyclo-

pentyl). A mixture of 12.07 g of 1,2,3,5-tetrahydro-5,9b-*o*-benzenobenz[*e*]isoindole (**22**, R = H),[2] 70 mL of chloroform, and 35 mL of triethylamine was treated with 10.5 g of cyclopentanecarbonyl chloride, keeping the temperature below 20 °C. After the mixture was stirred at room temperature for 2 h, 10% aqueous sodium hydroxide solution was added with cooling, and the mixture was stirred at room temperature for 30 min. The layers were separated, and the aqueous phase was extracted once with methylene chloride. Removal of the solvent from the dried extracts and crystallization of the residue from 50 mL of acetonitrile gave 13.14 g (77%) of 2-(cyclopentanecarbonyl)-1,2,3,5-tetrahydro-5,9b-*o*-benzenobenz[*e*]isoindole (**25**, R = cyclopentyl): NMR τ 2.5–3.5 (m, 9), 4.8 (d, J = 6 Hz, 1), 5.1 (s, 2), 5.8 (s, J = 2 Hz, 2), 6.7–8.7 (m, 9). An analytical sample (acetonitrile) had a melting point of 189–190 °C.

Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.04; H, 6.79; N, 4.29.

A mixture of 11.67 g of **25** (R = cyclopentyl) and 60 mL of trifluoroacetic acid was heated under reflux for 2 h. The excess acid was removed under vacuum, the residue was dissolved in methylene chloride, and the solution was poured into cold, stirred, excess aqueous sodium hydroxide solution. The mixture was extracted several times with methylene chloride, the extracts were dried, the solvent was removed, and the residue was crystallized from 40 mL of toluene to give 10.89 g (93%) of **26** (R = cyclopentyl): NMR τ 2.5–3.2 (m, 9), 5.0–6.1 (m, 3), 6.6–8.5 (m, 11). An analytical sample (acetonitrile) had a melting point of 185–186 °C.

Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.60; H, 6.93; N, 4.55.

2-(Cyclopentylmethyl)-2,3-dihydro-8*H*-3a,8-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyrrole (24, R = Cyclopentylmethyl) from 26. To a cooled slurry of 0.40 g of lithium aluminum hydride in 30 mL of ether was added 1.55 g of **26** (R = cyclopentyl), and the mixture was stirred at room temperature for 6 h. The excess hydride was decomposed by the addition of 0.4 mL of water, followed by 0.4 mL of 15% aqueous sodium hydroxide solution and 1.2 mL of water. The mixture was filtered, and the filtrate was concentrated. Crystallization of the residue from isopropyl alcohol gave 0.89 g (60%) of **24** (R = cyclopentylmethyl), identical by NMR and IR spectroscopy with a sample prepared from **22** by acid-catalyzed rearrangement as described above for **24** (R = Me). Compound **24** (R = cyclopentylmethyl) had the following: mp 103–104 °C; NMR τ 2.6–3.3 (m, 8), 3.9 (s, 1), 6.0–6.3 (d, J = 4 Hz, 1, and d, J = 10 Hz, 1), 6.8 (d, J = 10 Hz, 1), 7–9 (m, 13).

Anal. Calcd for $C_{24}H_{25}N$: C, 88.03; H, 7.70; N, 4.28. Found: C, 87.83; H, 8.06; N, 4.34.

2-(Cyclopentylmethyl)-2,3,8,12b-tetrahydro-*cis*-1*H*-3a,8-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyrrole (28, R = Cyclopentylmethyl). A mixture of 7.67 g of **26** (R = cyclopentyl), 100 mL of THF, and 2.1 g of 10% palladium on charcoal was shaken under 45 psi of initial hydrogen pressure at room temperature overnight. Removal of the solvent gave 6.76 g of 2-(cyclopentanecarbonyl)-2,3,8,12b-tetrahydro-*cis*-1*H*-3a,8-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyrrole (**28**, R = cyclopentylcarbonyl) as an oil. Crystallization from isopropyl alcohol produced a solid, mp 161–163 °C.

Anal. Calcd for $C_{24}H_{25}NO$: C, 83.93; H, 7.34; N, 4.08. Found: C, 84.24; H, 7.45; N, 4.33.

A mixture of 5.21 g of **28** (R = cyclopentylcarbonyl) and 1.2 g of lithium aluminum hydride was heated under reflux in THF for 3 h. The cooled mixture was treated, successively, with 1.2 mL of water, 1.2 mL of 15% sodium hydroxide solution, and 3.6 mL of water. Methylene chloride and magnesium sulfate were added, the mixture was filtered, and the filtrate was concentrated to give crude **28** (R = cyclopentylmethyl) as an oil that slowly solidified. It was converted to the hydrochloride (hydrogen chloride in ether) which after crystallization from 25 mL of 90% isopropyl alcohol weighed 3.49 g, mp ca. 265 °C dec.

Anal. Calcd for $C_{24}H_{28}ClN$: C, 78.77; H, 7.71; N, 3.83. Found: C, 78.84; H, 7.79; N, 3.89.

The NMR spectrum of the free base was as follows: τ 2.4–2.6 (m, 1, this signal was absent in the trans series), 2.7–3.3 (m, 7), 6.0 (d, J = 4 Hz, 1), 6.3–9.8 (m, 18). In the 220-MHz spectrum, the aliphatic region was resolved, from low to high field, as follows: d, J = 4 Hz, 1; dd, J = 7.5, 11 Hz, 1; d, J = 9 Hz, 1; m, 1; d, J = 9 Hz, 1; m, 3; dd, J = 4, 10 Hz, 1; d, J = 10 Hz, 1; m, 1; m, 8.

Base-Catalyzed Isomerization of 28 to 27. A mixture of **28** (R = cyclopentylmethyl; 0.68 g), 0.25 g of potassium *tert*-butoxide, and 4 mL of dry dimethyl sulfoxide was stirred under nitrogen at 87–88 °C (bath temperature) overnight. Dilution with water and extraction with benzene–ether gave 0.64 g of **27** (R = cyclopentylmethyl). Its 220-MHz NMR spectrum showed the starting material (**28**) to be completely absent. The product was identical with a sample of **27** (R = cyclopentylmethyl) prepared by catalytic hydrogenation (Pd/C, acetic acid) of **24** (R = cyclopentylmethyl). The hydrochloride of **27** (R = cyclopentylmethyl) had a melting point of 250–253 °C dec.

Anal. Calcd for $C_{24}H_{28}ClN$: C, 78.77; H, 7.71; N, 3.83. Found: C, 78.52; H, 7.83; N, 3.72.

2-Methyl-1,2,3,4,9,13b-hexahydro-*trans*-4a*H*-4a,9-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyridine (30, R = Me). A mixture of 5.00 g of 4,6-dihydro-3*H*-6,10b-*o*-benzenobenz[*h*]isoquinoline,[2] 80 mL of tetrahydrofuran, and 10 mL of methyl iodide was allowed to stand at room temperature for 5 h. The methiodide (7.68 g) so obtained was reduced with 2.4 g of sodium cyanoborohydride in 8 mL of glacial acetic acid and 80 mL of methanol at room temperature overnight. The excess hydride was destroyed with concentrated hydrochloric acid, and the mixture was made basic and extracted with methylene chloride. Removal of the solvent gave 4.92 g of crude 2-methyl-1,2,4,6-tetrahydro-3*H*-6,10b-*o*-benzenobenz[*h*]isoquinoline (**29**, R = Me). It was heated with 4.88 g of *p*-toluenesulfonic acid and 20 mL of glacial acetic acid in a Carius tube at 150 °C for 12 h. Most of the acetic acid was removed under vacuum, and the residue was dissolved in methylene chloride, washed with 15% aqueous sodium hydroxide solution, and dried. Removal of the solvent and crystallization from ethanol gave 3.43 g of 2-methyl-2,3,4,9-tetrahydro-4a,9-methano-4a*H*-dibenzo[3,4:6,7]-cyclohepta[1,2-*c*]pyridine, mp 141–142.5 °C. An analytical sample had the following: mp 142.5–143.5 °C; NMR τ 2.7–3.3 (m, 8), 3.5 (s, 1), 6.2 (d, J = 4 Hz, 1), 6.5–8.3 (m, 6), 7.4 (s, 3); UV (cyclohexane) λ_{max} 322 nm (ϵ 12 000).

Anal. Calcd for $C_{20}H_{19}N$: C, 87.87; H, 7.01; N, 5.12. Found: C, 87.55; H, 7.03; N, 4.89.

To a slurry of 3.28 g of the above product in 35 mL of methanol and 4 mL of acetic acid was added, with cooling, 1.56 g of sodium cyanoborohydride. After the mixture was stirred at room temperature overnight, the excess hydride was decomposed by stirring with 15 mL of concentrated hydrochloric acid for 2 h. The mixture was made basic and extracted with methylene chloride to give 3.43 g of an oil which slowly solidified. Crystallization from isopropyl alcohol gave 1.80 g of **30** (R = Me), mp 112–113 °C. An analytical sample had the following: mp 112–113 °C; NMR 2.5–3.0 (m, 8), 6.0 (d, J = 4 Hz, 1), 6.5–8.4 (m, 12).

Anal. Calcd for $C_{20}H_{21}N$: C, 87.22; H, 7.69; N, 5.09. Found: C, 87.23; H, 7.66; N, 5.10.

2-(Cyclopentylmethyl)-1,2,3,4,9,13b-hexahydro-*cis*-4a*H*-4a,9-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyridine (31, R = Cyclopentylmethyl). To a cooled, stirred mixture of 20.20 g of 4,6-dihydro-3*H*-6,10b-*o*-benzenobenz[*h*]isoquinoline,[2] 150 mL of methanol, and 20 mL of acetic acid was added, in small portions, 9 g of sodium cyanoborohydride. After the mixture was stirred at room temperature overnight, the excess hydride was decomposed by the slow addition of 100 mL of concentrated hydrochloric acid. The mixture was made basic and extracted with methylene chloride to give 20.27 g of crude 1,2,4,6-tetrahydro-3*H*-6,10b-*o*-benzenobenz[*h*]isoquinoline (**29**, R = H). A sample after crystallization from ethanol had the following: mp 168–169 °C dec; NMR τ 2.5–3.4 (m, 9), 5.0 (d, J = 6 Hz, 1), 6.9 (s, 2), 7.0 (t, split further, 2), 7.5 (t, split further, 2), 8.2 (s, 1).

Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.64; H, 6.68; N, 5.28.

A mixture of 1.57 g of **29** (R = H), 10 mL of THF, 2 g of magnesium oxide, and 2 mL of cyclopentanecarbonyl chloride was stirred at room temperature for 16 h. The mixture was filtered, the filtrate was concentrated to dryness, and the residue was dissolved in methylene chloride. The solution was washed with dilute hydrochloric acid and 15% aqueous sodium hydroxide solution, dried, and concentrated, leaving 1.88 g of crude 2-(cyclopentanecarbonyl)-1,2,4,6-tetrahydro-3*H*-6,10b-*o*-benzeno-

benz[*h*]isoquinoline (**29**, R = cyclopentanecarbonyl): NMR τ 2.6–3.4 (m, 9), 4.8–5.2 (m, 3), 6.5 (t, 2), 7.0–7.7 (m, 3), 7.7–8.7 (m, 8). A mixture of this product and 10 mL of trifluoroacetic acid was stirred at room temperature for 16 h. The acid was removed under vacuum, and the residue was dissolved in methylene chloride and made strongly basic with 15% aqueous sodium hydroxide solution. Removal of the solvent from the dried organic phase gave 1.70 g of 2-(cyclopentanecarbonyl)-2,3,4,9-tetrahydro-4a*H*-4a,9-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyridine as a solid: NMR τ 2.0–3.1 (m, 8), 5.1–8.5 (m, 16). This product was hydrogenated with Pd/C in tetrahydrofuran; the reaction was very slow and took about a week; addition of fresh catalyst was required. The product, crude 2-(cyclopentanecarbonyl)-1,2,3,4,9,13b-hexahydro-*cis*-4a*H*-4a,9-methanodibenzo[3,4:6,7]-cyclohepta[1,2-*c*]pyridine (**31**, R = cyclopentanecarbonyl), was heated under reflux with 0.5 g of lithium aluminum hydride in tetrahydrofuran for 2 h, giving 1.54 g of crude **31** (R = cyclopentylmethyl) as an oil that slowly solidified. The hydrochloride melted at ca. 310 °C dec after crystallization from ethanol.

Anal. Calcd for $C_{25}H_{30}ClN$: C, 79.02; H, 7.96; N, 3.69. Found: C, 79.29; H, 7.95; N, 3.72.

The NMR of the free base was as follows: τ 2.2–2.6 (m, 1), 2.7–3.2 (m, 7), 6.0–9.2 (m, 21). At 220 MHz, the aliphatic region is resolved, from low to high field, as follows: d, J = 4 Hz, 1; m, 2; m, 1; m, 1; m, 2; dd, J = 4, 10 Hz, 1; m, 5; m, 2; m, 4; m, 2.

2-Benzyl-1,2-dihydro-13b*H*-9,13b-methanodibenzo-[3,4:6,7]cyclohepta[1,2-*c*]pyridin-3(9*H*)-one (33, R = Benzyl). A solution of 9-anthraceneacetyl chloride, prepared as described before[2] from 35 g of 9-anthraceneacetic acid, in 80 mL of THF was added slowly with cooling to a mixture of 25 g of *N*-benzylpropargylamine, 40 mL of pyridine, and 220 mL of THF. The solvent was removed after stirring of the mixture at room temperature for 3 h, and the residue was washed with dilute ammonia, water, dilute hydrochloric acid, and dilute ammonia and dried. The solid so obtained was heated under reflux with 300 mL of *p*-xylene for 90 min. The solvent was removed, and the residue (crude **32**, R = benzyl) was heated under reflux with 200 mL of acetic acid and 50 g of *p*-toluenesulfonic acid for 26 h. The solvent was removed, the residue was dissolved in methylene chloride, and the solution was washed with 15% sodium hydroxide solution. Removal of the solvent from the dried solution and crystallization of the residue from dimethylformamide gave 30.5 g (61%) of **33** (R = benzyl): mp 216–217 °C; NMR τ 2.2–3.1 (m, 13), 3.6 (s, 1), 4.9 (d, J = 14 Hz, 1), 5.3 (d, J = 14 Hz, 1), 6.5 (d, J = 4 Hz, 1), 6.5–7.0 (AB q, $J \approx 12$ Hz, 2), 8.1 (dd, J = 4, 10 Hz, 1), 8.4 (d, J = 10 Hz, 1).

Anal. Calcd for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99. Found: C, 85.28; H, 5.87; N, 4.02.

2-Benzyl-1,2,3,4,4a,9-hexahydro-*cis*-13b*H*-9,13b-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyridine (35, R = Benzyl). A mixture of 15.4 g of **33** (R = benzyl), 50 mL of THF, 50 mL of acetic acid, and 2.7 g of 10% Pd/C was shaken in a Parr shaker under 50 psi of hydrogen for 3.5 days. The solvents were removed from the filtered solution, the residue was dissolved in methylene chloride, and the solution was washed with dilute sodium hydroxide solution. Removal of the solvent from the dried solution gave 15.2 g of crude 2-benzyl-1,2,4a,9-tetrahydro-*cis*-13b*H*-9,13b-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyridin-3(4*H*)-one (**34**, R = benzyl). Reduction of this product with 2 g of lithium aluminum hydride (THF, reflux, 4 h) and crystallization of the crude product from acetonitrile gave 9.2 g (63%) of **35** (R = benzyl), mp 119–119.5 °C. An analytical sample had the following: mp 119.5 °C; NMR (220 MHz) τ 1.5 (d, J = 7.5 Hz, 1), 2.3–3.0 (m, 12), 6.0 (d, J = 4 Hz, 1), 6.3 (s, 2), 6.7 (d, J = 11 Hz, split further, 1), 6.8 (d, J = 11 Hz, 1), 7.0 (dd, J = 12, 3 Hz, 1), 7.5 (d, J = 11 Hz, 1), 7.6–7.9 (m, 4), 8.2 (m, 1).

Anal. Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.13. Found: C, 88.53; H, 7.16; N, 3.86.

2-Benzyl-1,2,3,4,4a,9-hexahydro-*trans*-13b*H*-9,13b-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyridine (36, R = Benzyl). A mixture of 2.53 g of **35** (R = benzyl), 1.30 g of potassium *tert*-butoxide, and 200 mL of dry dimethyl sulfoxide was stirred in a 100 °C oil bath for 60 h. The semisolid obtained on dilution with water weighed 2.58 g. The NMR spectrum showed the presence of the isomers **35** and **36** in a ratio of 25:75. The product was converted to the hydrochloride which after crystallization from 90% ethanol had a melting point of 300–305 °C dec.

Anal. Calcd for $C_{25}H_{26}ClN$: C, 79.87; H, 6.97; N, 3.73. Found: C, 79.93; H, 6.86; N, 3.48.

The NMR spectrum of the free base (220 MHz) was as follows: τ 2.3–3.0 (m, 13), 6.0 (d, J = 4.5 Hz, 1), 6.2 (d, J = 13.5 Hz, 1), 6.4 (d, J = 13.5 Hz, 1), 6.9 (d, J = 11 Hz, split further, 1), 7.0 (dd, J = 11, 2 Hz, 1), 7.2 (2 d, J = 11 Hz, 2), 7.4 (dd, J = 11, 5 Hz, 1), 7.6 (td, J = 11, 3 Hz, 1), 7.7–8.6 (m, 3).

The stereochemical assignment is based on comparison of the aromatic region with that of the five-membered analogues **27** and **28** (R = cyclopentylmethyl). Only the cis compounds **28** and **35** have a single proton at lower field than the rest of the aromatic protons. Inspection of models shows that the aromatic hydrogen ortho to the quaternary carbon atom is 2.7 Å from the deshielding nitrogen in the cis compound **28** and 2.0 Å from it in the cis compound **35**. By contrast, the distances are 4.0 and 4.3 Å, respectively, in the trans compounds **27** and **36**.

1,2,8,12b-Tetrahydro-3*H*-3a,8-methanodibenzo[3,4:6,7]-cyclohepta[1,2-*b*]pyrrole (38). Chlorosulfonyl isocyanate (4.4 mL) was added under nitrogen to a solution of 5.0 g of 11-methylene-9,10-dihydro-9,10-ethanoanthracene[13] in 20 mL of acetonitrile, and the mixture was stirred at room temperature for 5 h. The crystals were collected after cooling of the mixture with ice, washed with cold ether, and dried to give 4.05 g (49%) of 1-(chlorosulfonyl)-8,12-dihydro-3*H*-3a,8-methanodibenzo-[3,4:6,7]cyclohepta[1,2-*b*]pyrrol-2(1*H*)-one. This product was stirred with 80 mL of methylene chloride and 70 mL of a solution of sodium hydroxide (10%) and sodium sulfite (10%) at room temperature for 18 h. From the organic layer there was obtained 2.68 g of crude 8,12b-dihydro-3*H*-3a,8-methanodibenzo[3,4:6,7]-cyclohepta[1,2-*b*]pyrrol-2(1*H*)-one (**37**). An analytical sample (dimethylformamide) had the following: mp 273 °C; NMR τ 2.0 (br s, 1), 2.4–3.2 (m, 8), 5.7 (s, 1), 6.1 (d, J = 4 Hz, 1), 6.8 and 7.7 (AB q, 2), 7.7–7.9 (m, 2).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.38. Found: C, 82.70; H, 5.86; N, 5.44.

The above crude lactam **37** (2.85 g) was reduced with 0.76 g of lithium aluminum hydride in refluxing tetrahydrofuran for 4.5 h to give 2.54 g of the crude **38** (R = H) as a solid. Crystallization of 0.98 g of this product from acetonitrile gave 0.69 g of pure product: mp 147–148 °C; NMR τ 2.6–3.1 (m, 8), 6.1 (d, J = 4.5 Hz, 1), 6.3 (s, 1), 6.6–8.4 (m, 7). The latter, at 220 MHz, is resolved from low to high field as follows: m, 2; m, 1; br s, 1; dd, J = 4.5, 10 Hz, 1; d, J = 10 Hz, 1; m, 1.

Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.01; H, 7.04; N, 5.69.

1-Methyl-1,2,8,12b-tetrahydro-3*H*-3a,8-methanodibenzo-[3,4:6,7]cyclohepta[1,2-*b*]pyrrole (38, R = Me). A mixture of 1.67 g of crude **38** (R = H), 10 mL of formic acid, and 10 mL 40% formaldehyde solution was heated under reflux for 4 h. Concentrated hydrochloric acid (5 mL) was added to the cooled mixture which was then concentrated. The residue was made basic and extracted with methylene chloride to give 1.71 g of the crude product which on crystallization from isopropyl alcohol gave 1.01 g of **38** (R = Me), mp 114–115 °C, which was unchanged on further recrystallization: NMR τ 2.6–3.1 (m, 8), 6.1 (d, J = 4.5 Hz, 1), 6.5–8.4 (m, 10).

Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36. Found: C, 86.95; H, 7.33; N, 5.42.

Registry No. **1a**, 72917-62-5; **1b**, 72917-65-8; **1c**, 56948-79-9; **2a**, 72925-81-6; **2b**, 72925-82-7; **2c**, 56949-09-8; **3**, 56948-81-3; **4**, 57290-70-7; **5**, 72925-83-8; **6**, 72925-84-9; **7**, 56948-83-5; **8**, 56949-08-7; **9**, 56949-07-6; **10**, 72917-45-4; **10**·HCl, 56949-20-3; **11**, 56949-19-0; **12a**, 72917-46-5; **12b**, 72917-47-6; **12b**·HCl, 72917-48-7; **13a**, 72917-49-8; **13b**, 72917-50-1; **13b**·HCl, 72917-51-2; **18a**, 72917-52-3; **18b**, 72917-53-4; **19a**, 72917-54-5; **19b**, 72917-55-6; **19b** maleate, 72917-56-7; **20**, 57446-98-7; **21**, 57446-99-8; **22** (R = H), 56948-82-4; **22** (R = Me), 56948-83-5; **24** (R = Me), 57447-01-5; **24** (R = cyclopentylmethyl), 57447-14-0; **25** (R = cyclopentyl), 57475-87-3; **26** (R = cyclopentyl), 57447-15-1; **27** (R = Me), 57447-00-4; **27** (R = Me) HCl, 57495-87-1; **27** (R = cyclopentylmethyl), 57447-12-8; **27** (R = cyclopentylmethyl) HCl, 57495-83-7; **28** (R = cyclopentylcarbonyl), 57447-16-2; **28** (R = cyclopentylmethyl), 72982-86-6; **28** (R = cyclopentylmethyl) HCl, 73035-72-0; **29** (R = H), 72917-57-8; **29** (R = Me), 72917-13-6; **29** (R

= cyclopentanecarbonyl), 72917-14-7; **30** (R = Me), 72917-15-8; **31** (R = cyclopentanecarbonyl), 72917-16-9; **31** (R = cyclopentylmethyl), 72917-17-0; **31** (R = cyclopentylmethyl) HCl, 72982-83-3; **32** (R = benzyl), 72917-18-1; **33** (R = benzyl), 72917-19-2; **34** (R = benzyl), 72917-20-5; **35** (R = benzyl), 72917-21-6; **35** (R = benzyl) HCl, 72982-84-4; **36** (R = benzyl), 72982-85-5; **36** (R = benzyl) HCl, 73035-71-9; **37**, 72917-22-7; **38** (R = H), 72917-23-8; **38** (R = Me), 72917-24-9; spiro[5*H*-5,9b-*o*-benzenobenz[*e*]isoindole-3,1′-cyclohexane], 72917-25-0; spiro[cyclohexane-1,1′(3*H*)-2*H*-dibenzo[3,4:7,8]cycloocta[1,2-*c*]pyrrole], 72917-26-1; cyclopentanecarbonyl chloride, 4524-93-0; 4,6-dihydro-3*H*-6,10b-*o*-benzenobenz[*h*]isoquinoline, 72917-27-2; 2-methyl-2,3,4,9-tetrahydro-4a,9-methano-4a*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyridine, 72917-28-3; 2-(cyclopentanecarbonyl)-2,3,4,9-tetrahydro-4a*H*-4a,9-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyridine, 72917-29-4; 9-anthraceneacetyl chloride, 72917-30-7; *N*-benzylpropargylamine, 1197-51-9; 11-methylene-9,10-dihydro-9,10-ethanoanthracene, 19978-14-4; 1-(chlorosulfonyl)-8,12-dihydro-3*H*-3a,8-methanodibenzo[3,4:6,7]cyclohepta[1,2-*b*]pyrrol-2(1*H*)-one, 72925-73-6; chlorosulfonyl isocyanate, 1189-71-5.

Notes

Intramolecular Diels–Alder Additions. 3. Additions to Isoindole

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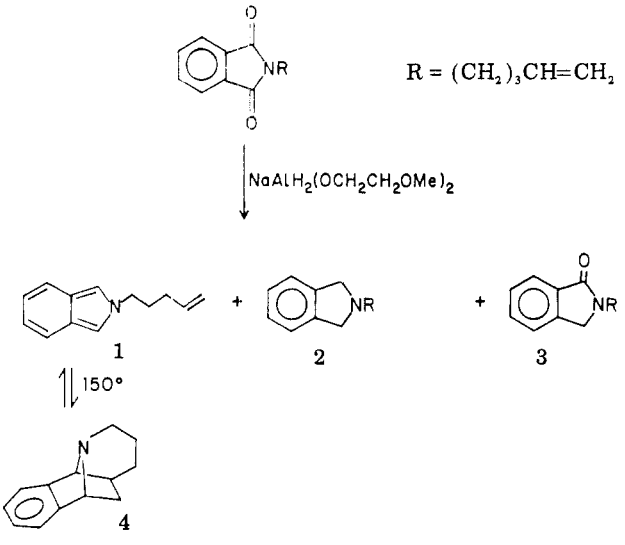
Received October 16, 1978

In the first two papers[1] of this series, we described intramolecular Diels–Alder additions to anthracene and acridine and some rearrangements of 9,12-bridged ethenoanthracenes. In this note we report an intramolecular Diels–Alder addition to isoindole.[2]

N-4-Pentenylisoindole (**1**) was prepared by reduction of *N*-4-pentenylphthalimide with sodium bis(2-methoxyethoxy)aluminum hydride.[3] The desired product was contaminated by the isoindoline **2** and the isoindolinone **3**.



Removal of **2** by acid extraction left a mixture of ca. 70% of the isoindole **1** and 30% of **3**. Heating this mixture in toluene to 150 °C for 8 h resulted in partial cyclization of **1** to 1,2,3,4,6,10b-hexahydro-1,6-methanopyrido[2,1-*a*]isoindole (**4**); the ratio of **1** and **4**, as determined by NMR spectroscopy, was ca. 1:1. At 200 °C under otherwise identical conditions, the ratio of **1** and **4** was about 2.3:1, indicating that at elevated temperatures **1** and **4** were in equilibrium. Slow fractional distillation of the equilibrium mixture at 160–180 °C (bath temperature) resulted in almost complete conversion to the lower boiling cyclized isomer **4**. No cyclization was observed in the case of *N*-5-hexenylisoindole [$(CH_2)_4CH{=}CH_2$ in place of pentenyl group on **1**].

Experimental Section

***N*-4-Pentenylisoindole (1).** A mixture of 32.5 g of potassium phthalimide, 33 g of 5-bromo-1-pentene, and 150 mL of anhydrous dimethylformamide was stirred at 127 °C (bath temperature) overnight. Most of the solvent was removed under vacuum. Ice was added to the residue, and the product was collected by filtration, washed with water, and dried to give 35.79 g of crude *N*-4-pentenylphthalimide as a low-melting solid; it was used without further purification.

A 70% solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene (100 mL) was added over a period of 45 min to a mechanically stirred solution of 28.5 g of *N*-4-pentenylphthalimide in 180 mL of benzene, keeping the temperature at 15–20 °C. After being stirred at room temperature for 1 h, the mixture was cooled, and 100 mL of a 25% aqueous sodium hydroxide solution was added slowly. The layers were separated, and the aqueous phase was extracted twice with benzene. The combined organic phases were washed with water and then extracted with several portions of 5% sulfuric acid to remove the *N*-4-pentenylisoindoline (**2**, 9.3 g after reconversion to the free base). Removal of the solvent gave 13.2 g of a dark liquid consisting of ca. 70% of *N*-4-pentenylisoindole (**1**) and 30% of *N*-4-pentenylisoindolin-1-one (**3**). It was short-path distilled (95–150 °C bath temperature, 0.5 μm) to give 10.43 g of a yellow liquid, still containing most of the isoindolinone impurity. The products had the following NMR spectra (in $CDCl_3$). For **1**: τ 2.5–3.5 (m, 6), 3.9–4.8 (m, 1), 4.9–5.4 (m, 2), 6.1 (t, J = 6.5 Hz, 2), 8.0–8.6 (m, 4). For **2**: τ 3.0 (s, 4), 2.9–3.5 (m, 1), 4.8–5.2 (m, 2), 6.2 (s, 4), 7.4 (t, J = 7 Hz, 2), 7.7–8.6 (m, 4). For **3**: τ 2.3–3.4 (m, 4), 4.0–4.7 (m, 1), 5.0–5.4 (m, 2), 5.9 (s, 2), 6.6 (t, J = 7 Hz, 2), 7.8–9.0 (m, 4).

1,2,3,4,6,10b-Hexahydro-1,6-methanopyrido[2,1-*a*]isoindole (4). The crude *N*-4-pentenylisoindole (**1**) was distilled slowly through a spinning-band column at 160–180 °C (bath temperature) (0.3 mm), giving 7.41 g (80%) of essentially pure **4** in four fractions: bp 90–92 °C (0.3 mm); n^{24}_D 1.5745–1.5773. The purest fraction had the following: n^{24}_D 1.5765; NMR (in $CDCl_3$) τ 2.8–3.2 (m, 4), 5.8 (d, J = 4.5 Hz, 1), 6.1 (s, 1), 6.8–7.2 (m, 2), 7.9–9.1 (m, 7). The methiodide melted at 147–147.5 °C dec after crystallization from isopropyl alcohol: NMR (in $CDCl_3$) τ 2.3–2.8 (m, 4), 4.1 (d, J = 4 Hz, split further, 1), 4.3 (s, slightly split, 1), 5.5–6.1 (m, 2), 6.9 (s, 3), 7.1–9.1 (m, 7).

Anal. Calcd for $C_{14}H_{18}IN$: C, 51.39; H, 5.51; N, 4.28. Found: C, 51.53; H, 5.59; N, 4.30.

(1) Parts 1 and 2, E. Ciganek, *J. Org. Chem.*, companion papers in this issue.

(2) For intermolecular Diels–Alder additions to isoindoles, see: J. C. Emmett and W. Lwowski, *Tetrahedron*, **22**, 1011 (1966); J. E. Shields and J. Bornstein, *Chem. Ind. (London)*, 1404 (1967).

(3) D. I. Garmaise and A. Ryan, *J. Heterocycl. Chem.*, 413 (1970).

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