Intramolecular Diels–Alder Additions. 1. Additions to Anthracene and Acridine[1]

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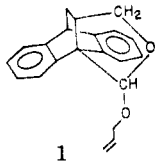
Intramolecular Diels–Alder reaction of suitably 9-substituted anthracenes at temperatures ranging from 25 to 220 °C yields a wide variety of 9,12-bridged ethano- and ethenoanthracenes. Adducts having three-, four-, and five-membered bridges, many incorporating heteroatoms such as oxygen, nitrogen, and sulfur, have been prepared. The ease of cyclization decreases with increasing bridge length. Neither the diene nor the dienophile need to carry activating groups; vinyl and ethynyl dienophiles add with equal ease. Cyclization of *N*-methyl-*N*-propargyl-9-acridinecarboxamide gives **31**, the first thermal [4 + 2] adduct of an acridine.

The intramolecular Diels–Alder reaction provides a simple and direct approach to complex polycyclic compounds. Two rings are formed in a single step, and the cyclization often proceeds under remarkably mild conditions. Early examples of this reaction were mostly the result of accidental observations. A systematic study of its synthetic applications has begun only recently.[2] We were interested in exploring the potential of this reaction for the preparation of compounds having useful properties as therapeutic agents, especially for diseases of the central nervous system. This paper describes intramolecular Diels–Alder reactions involving the central ring of anthracene and acridine as the diene.

Anthracene is a fairly reactive diene, and many intermolecular adducts have been prepared; on the other hand, no thermal [4 + 2] cycloadditions of acridine appear to have been reported.[3] An intramolecular Diels–Alder reaction of an anthracene derivative was reported by Meek and Dann,[4a] who obtained the cyclic acetal **1** in 2% yield



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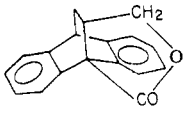

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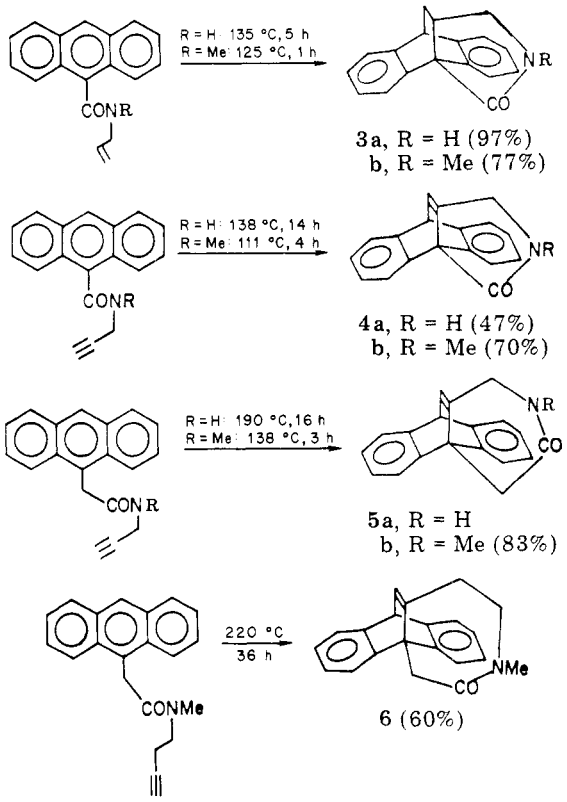
on attempted preparation of 9-anthraldehyde diallyl acetal. Cyclization of the intermediate allyl 9-anthroate was considered as one of the possible mechanisms for the formation of the lactone **2** from 9-anthramide and allyl alcohol.[4b]

Results

A wide variety of 9,12-bridged ethano- and ethenoanthracenes have been obtained by cyclization of suitably 9-substituted anthracenes. These include amides (Scheme I), imines (Scheme II), amines (Scheme III), ethers, thioethers, esters, and acetals (Scheme IV), and carbinols (Scheme V). The reactions were monitored by NMR spectroscopy, and the reaction times and temperatures given are usually those required for complete disappearance of the starting materials. Yields have not been optimized in all cases; lower yields were often due to difficulties with isolation rather than side reactions. The products are thermally stable and can be distilled or sublimed under reduced pressure without undergoing retrograde Diels–Alder reaction. Structures were assigned on the basis of their NMR spectra.

Scheme I



(1) Some of the compounds described in this paper are claimed in a U.S. Patent: E. Ciganek, U.S. Patent 4 077 977 (1978).

(2) For reviews of the intramolecular Diels–Alder reaction, see: H. Wollweber in *Methoden Org. Chem. (Houben-Weyl), 4th Ed.*, **5/1c**, 1113 (1970); R. G. Carlson, *Annu. Rep. Med. Chem.*, **9**, 270 (1974); W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, **16**, 10 (1977).

(3) For photochemical [4 + 2] cycloadditions to acridine, see: N. C. Yang, K. Srinivasachar, B. Kim, and J. Libman, *J. Am. Chem. Soc.*, **97**, 5006 (1975); T. Sasaki, K. Kanematsu, I. Ando, and O. Yamashita, *ibid.*, **99**, 871 (1977). For attempted thermal Diels–Alder reactions of acridines, resulting in formation of dihydroacridines instead, see: R. M. Acheson and M. L. Burstal, *J. Chem. Soc.*, 3240 (1954); R. M. Acheson and J. Woollard, *J. Chem. Soc., Perkin Trans. 1*, 438 (1975). Benzo[*b*]acridine adds dienophiles at the carbocyclic ring or gives dihydro derivatives analogous to acridine: R. M. Acheson and C. W. Jefford, *J. Chem. Soc.*, 2676 (1956). The addition of dehydronaphthalene to acridine *N*-oxide has been reported by G. Wittig and G. Steinhoff, *Chem. Ber.*, **95**, 203 (1962).

(4) (a) J. S. Meek and J. R. Dann, *J. Org. Chem.*, **21**, 968 (1956); (b) J. S. Meek, D. R. Wilgus, and J. R. Dann, *J. Am. Chem. Soc.*, **82**, 2566 (1960).

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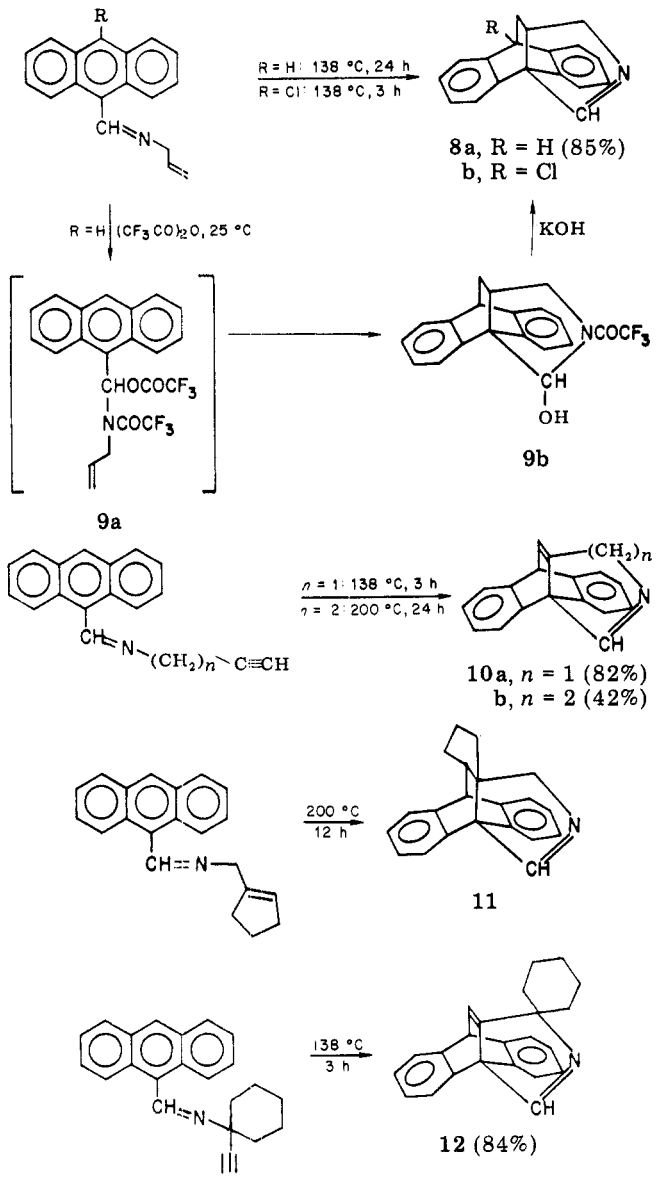
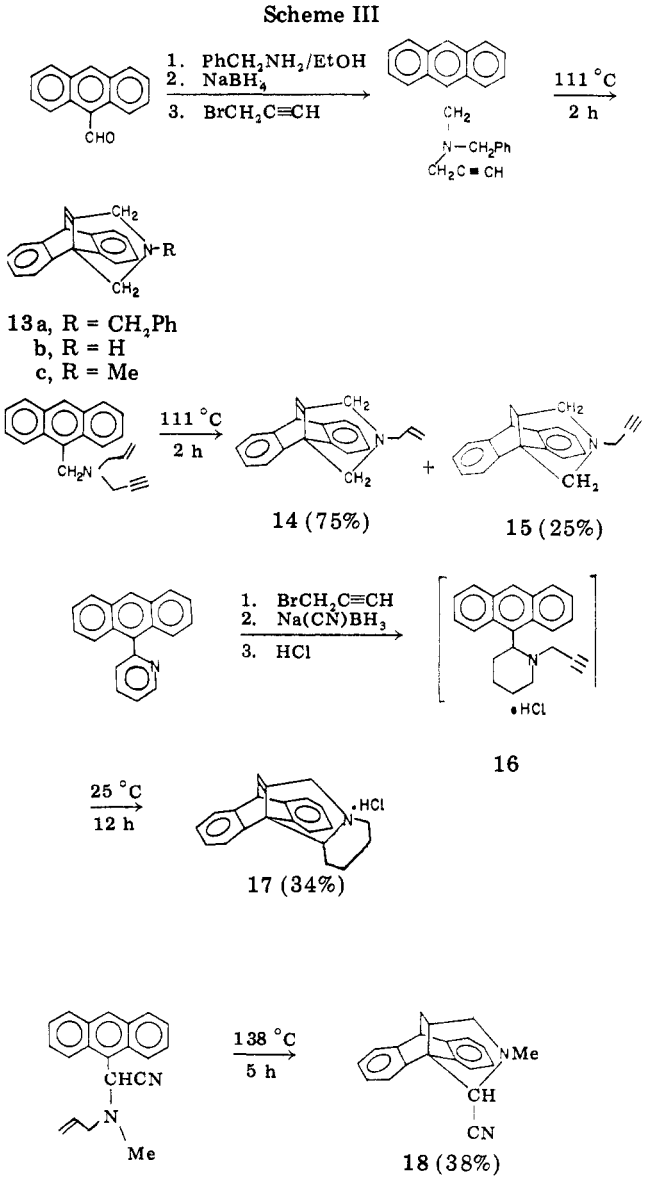
Scheme II



Scheme III



Amides. Heating *N*-allyl- and *N*-propargylamides derived from commercially available 9-anthracenecarboxylic acid produced γ-lactams as shown in Scheme I; analogously, δ-lactams were obtained from 9-anthraceneacetic acid. *N*-Butynylamides of the latter produced seven-membered lactams as illustrated for compound **6**. The thermodynamic parameters of the first-order cyclization of *N*-methyl-*N*-propargyl-9-anthramide to lactam **4b** were determined by measuring the rates at four temperatures between 80 and 111 °C. Benzene, toluene, and mixtures of the two solvents were employed for experimental reasons, but although a single solvent would have been preferable, a good Arrhenius plot was obtained. The activation energy was found to be 23.9 ± 0.4 kcal/mol and the activation entropy (calculated for 111 °C) −11 eu. The corresponding *N*-benzylamide cyclized at a somewhat faster rate (the first-order half-life was 11 min at 111 °C compared to 30 min for the *N*-methyl analogue).

Imines. Cyclization of the *N*-allyl- and *N*-propargylimines of 9-anthraldehyde (Scheme II) occurred at somewhat higher temperature than that of the corresponding amides, possibly because the necessary conversion of the trans to the cis imines prior to cycloaddition required additional energy. Treatment of 9-anthraldehyde *N*-allylimine with trifluoroacetic anhydride at room temperature followed by workup with aqueous base produced the amide **9b** in 25% yield. Imines are known to add the elements of trifluoroacetic anhydride readily, and it is probably the adduct **9a** that undergoes the intramolecular Diels–Alder reaction. Treatment of amide **9b** with hot alkali produced the cyclic imine **8a**.

Amines. Cyclization of a variety of *N*-allyl- and *N*-propargylanthracenemethanamines is illustrated in Scheme III. The former gave 1,2,3,3a,4,5-hexahydro-5,9b-*o*-benzenobenz[*e*]isoindoles (e.g., **15** and **18**). Compounds of that ring system have also been prepared recently by intermolecular Diels–Alder reaction followed by cyclization.[12] The most convenient method for the preparation of 1,2,3,5-tetrahydro-5,9b-*o*-benzenobenz[*e*]isoindoles **13**, which are substrates for various photochemical and acid-catalyzed rearrangements,[7] is shown for the 2-

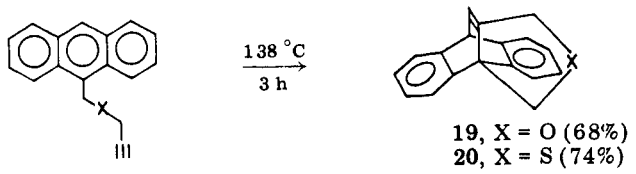
(5) J. C. Muller and J. Vergne, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **263**, 1452 (1966).

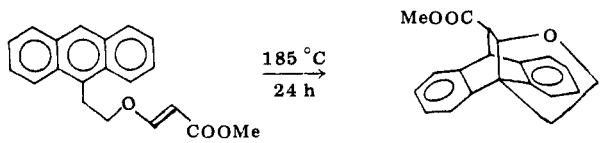
(6) For other examples of imine–enamine tautomerisms, see H. Quast and H. Heublein, *Chem. Ber.*, **108**, 2574 (1975), and references cited therein.

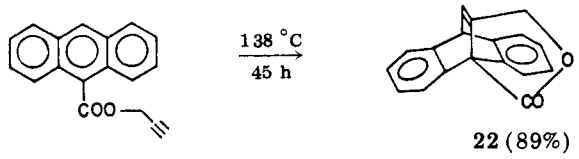
(7) See paper 2 in this series: E. Ciganek, *J. Org. Chem.*, companion paper in this issue.

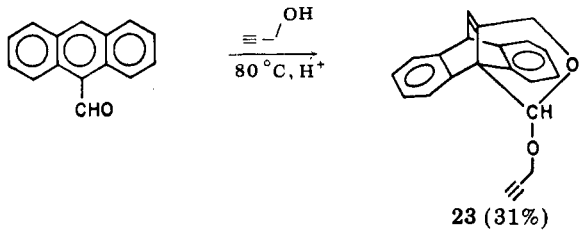
(8) It is important to use 9-anthraldehyde that is free of anthracene since the latter often is difficult to remove and may even be enriched in the course of a synthetic sequence.

Scheme IV

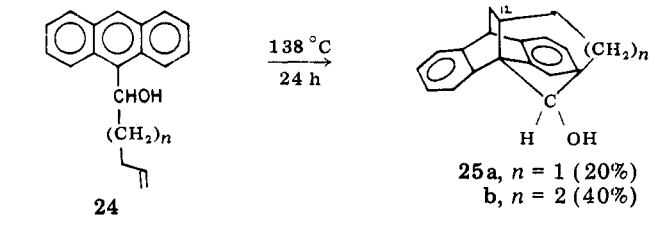


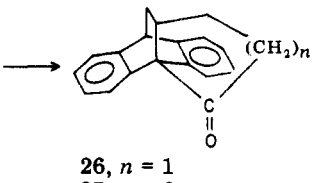






Scheme V



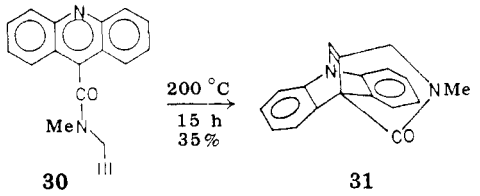


benzyl derivative **13a**. Reaction of 9-anthraldehyde with benzylamine in boiling ethanol followed by in situ borohydride reduction of the intermediate imine gave *N*-benzyl-9-anthracenemethanamine. Alkylation with propargyl bromide in methylene chloride/aqueous sodium hydroxide solution at room temperature produced only a small amount of undesired quaternary ammonium bromide; the main product was the tertiary propargylamine which was cyclized by heating under reflux in toluene. None of the intermediates needed to be purified, and the overall yield of **13a** from 9-anthraldehyde was 76%. Alternatively, the cyclic imines **10** (Scheme II) were reduced with sodium cyanoborohydride in acetic acid to the parent amines (e.g., **13b**) which could then be acylated or alkylated. Hydride reduction of the lactams (Scheme I) often produced carbinolamines, especially in the smaller ring sizes. Methylation of the cyclic imines **10** or the parent amines (e.g., **13b**) under Clarke–Eschweiler conditions gave the *N*-methyl tertiary amines (e.g., **13c**).

Ethers, Thioethers, Esters, and Acetals. Although the main emphasis of this work was on the synthesis of nitrogen heterocycles, we have also demonstrated the utility of the intramolecular Diels–Alder addition to anthracenes for the preparation of oxygen- and sulfur-containing rings (Scheme IV).

Carbinols. Addition of the appropriate Grignard reagents to 9-anthraldehyde produced the carbinols **24** which on heating gave the cyclized alcohols **25**. Only one of the two possible isomers was isolated in each case, and inspection of the NMR spectra of the crude products showed little or none of the other isomer to be present. The structures are tentatively assigned as shown in Scheme V (OH and H on C-12 trans) since models indicate serious steric crowding between the hydroxyl group and the *peri*-hydrogen atom in the conformer leading to the other isomer. Oxidation of the alcohols yielded the ketones **26** and **27**. Reaction of the cyclopentanone **26** with methylamine gave the expected imine **28**. On the other hand, the product obtained from the cyclohexanone **27** exists predominantly in the secondary enamine form, **29** (in $CDCl_3$), possibly to relieve steric interaction between the methylene group adjacent to the imine carbon and the *peri*-hydrogen. No enol was detected in ketone **27**.[6]

Acridine. Intramolecular Diels–Alder additions to the central ring of acridine proceeded with much greater difficulty. This was not surprising, since attempted intermolecular Diels–Alder additions to acridine either have been unsuccessful or have produced unbridged dihydroacridines.[3] Cyclization of *N*-methyl-*N*-propargyl-9-acridinecarboxamide (**30**) required heating to 200 °C. The corresponding allylamide was recovered unchanged under these conditions.



Discussion

The results presented above show that intramolecular Diels–Alder additions to anthracenes are quite general. As found in other systems,[2] the rates of cyclization depend strongly on the length and nature of the chain connecting

(9) F. A. Vingiello and M. M. Schlechter, *J. Org. Chem.*, **28**, 2448 (1963).

(10) B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 420 (1948).

(11) K. Lehmstedt and E. Wirth, *Ber. Dtsch. Chem. Ges.*, **61**, 2044 (1928).

(12) W. E. Hahn, R. Bartnik, W. Szalecki, and W. Kalczynski, *Rocz. Chem.*, **51**, 2315 (1977); W. E. Hahn and W. Szalecki, *Pol. J. Chem.*, **52**, 2215 (1978).

the diene and dienophile and to some extent on the nature of the substituents on both the diene and dienophile. In general, ease of cyclization decreases as the chain is lengthened from three to five atoms. Presumably, with longer chains the entropy advantage of the intramolecular Diels–Alder reaction is gradually lost. Thus, cyclization of *N*-(3-butynyl)-*N*-methyl-9-anthraceneacetamide to the seven-membered lactam **6** requires conditions (220 °C) that approach those necessary for the intermolecular Diels–Alder addition of acetylene to anthracene (250 °C).[5] Although fused cyclopropanes and cyclobutanes have been obtained[2] from substrates where the diene and dienophile are separated by one- and two-atom chains, such small rings fused to the 9- and 12-position of ethanoanthracenes would be energetically unfavorable. The single attempt made in this direction, cyclization of the carbinol **24** (n = 1), was therefore predictably unsuccessful. Substituents on the chain have a pronounced influence on the cyclization rates since bulky groups may increase the population of the conformer leading to the transition state (i.e., having the dienophile above the diene).[13] Dramatic illustrations of this effect are provided by the cyclizations of intermediates **9a** (Scheme II) and **16** (Scheme III) at room temperature. Secondary amides invariably require higher cyclization temperatures than tertiary amides.[13] Tertiary amides (Scheme I) and tertiary amines (Scheme III) cyclize with comparable rates. The fact that the inductive effect of a carbonyl group on the diene, if anything, slightly inhibits the rate of reaction is also illustrated by the observation that 9-anthracenemethyl propargyl ether cyclizes somewhat more readily than propargyl 9-anthroate (Scheme IV). This rate difference may also be due to the slightly larger bond angle of the carbonyl group. A resonance effect is presumably negligible since in the transition state the carbonyl group is twisted out of the diene plane. A chlorine substituent on the terminus of the diene enhances the rate of cyclization (**8b**, Scheme II). There is little difference between the rates of addition of a terminal ethylene and a terminal acetylene to anthracenes. *N*-Allyl-9-anthramides cyclize as readily as *N*-propargyl-9-anthramides (Scheme I). However, the bridged ethenoanthracene **14** slightly predominates among the cyclization products of *N*-allyl-*N*-propargyl-9-anthracenemethanamine (Scheme III). The dienophile may carry a substituent (e.g., **21**, Scheme IV) or be part of a ring (e.g., **11**, Scheme II). As a consequence of the constraints imposed by the bridge, all cyclizations reported here are regiospecific in giving 9,12-fused ethano- and ethenoanthracenes exclusively, whereas intermolecular Diels–Alder additions of unsymmetrical dienophiles to 9-substituted anthracenes often produce mixtures of both regioisomers.[14]

The activation entropy for the formation of lactam **4b** (−11 eu) is, as expected, considerably less negative than the activation entropies encountered in intermolecular Diels–Alder reactions which are in the range of −35 eu. This is a consequence of the fewer degrees of freedom in the substrates for the intramolecular cyclization.[15]

Experimental Section

Unless otherwise noted, all NMR spectra were determined in $CDCl_3$ solution. Yields have not always been optimized. **Caution**: benzene and dioxane are believed to be carcinogenic.

3,3a,4,5-Tetrahydro-5,9b-*o*-benzenobenz[*e*]isoindol-1-(2*H*)-one (3a). The following procedure is the general method for the preparations of the lactams in Scheme I.

A mixture of 18.85 g of 9-anthroic acid and 60 mL of thionyl chloride was heated under reflux for 1 h. The excess reagent was removed under vacuum (30 mm; 90 °C bath temperature), toluene (50 mL) was added, and the mixture was concentrated again. This operation was repeated once more to give 20.6 g of 9-anthroyl chloride as a very moisture-sensitive, yellow solid.

A solution of 6.76 g of 9-anthroyl chloride in 20 mL of tetrahydrofuran (THF) was added, at 10–15 °C, to a solution of 30 mL of allylamine in 50 mL of THF. After the mixture was stirred at room temperature for 4 h, the solvent was removed, and the residue was stirred with methylene chloride and 5% aqueous sodium bicarbonate solution. The methylene chloride layer was dried and concentrated, and the residue was crystallized from 70 mL of ethanol to give 4.76 (65%) of *N*-allyl-9-anthramide, mp 195–196 °C. An analytical sample had the following: mp 195–196 °C; NMR τ 1.6–2.8 (m, 9), 3.5–5.1 (m, 4), 5.9 (t, 2).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.76; N, 5.36. Found: C, 82.88; H, 5.92; N, 5.26.

A mixture of 2.31 g of *N*-allyl-9-anthramide and 20 mL of *p*-xylene was heated under reflux for 5 h. A precipitate started forming after 2 h. As the mixture cooled, 2.24 g (97%) of the title compound, mp 234–235 °C, was obtained. An analytical sample had the following: mp 235–236 °C; NMR τ 2.0–3.0 (m, 8), 3.7 (br, 1), 5.7 (t, 1), 6.5–6.8 (m, 1), 7.3–8.8 (m, 4).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.62; H, 5.75; N, 5.12.

2-Methyl-3,3a,4,5-tetrahydro-5,9b-*o*-benzenobenz[*e*]isoindol-1(2*H*)-one (3b). *N*-Allyl-*N*-methyl-9-anthramide was obtained as an oil, the NMR spectrum of which indicated the presence of two rotamers: τ 1.5–3.0 (m, 9), 4.0–5.1 (m, 3.1), 5.6 (d, split further, 1.0), 6.5 (d, split further, 0.9), 6.7 (s, 1.2), 7.4 (s, 1.4). The product cyclized on attempted molecular distillation.

A mixture of 4.08 g of crude *N*-allyl-*N*-methyl-9-anthramide and 40 mL of *p*-xylene was stirred at 125 °C (inside temperature) for 1 h. As the mixture cooled, 3.25 g (77%) of **3b** precipitated. An analytical sample (acetonitrile) had the following: mp 206–208 °C; NMR τ 2.0–2.3 (m, 1), 2.6–3.0 (m, 7), 5.6 (dd, J = 3.5, 1 Hz, 1), 6.7 (dd, J = 9, 6.5 Hz, 1), 7.5 (dd, J = 10, 9 Hz, 1), 7.7 (m, 1), 8.0 (ddd, J = 12, 10, 3.5 Hz, 1), 8.6 (ddd, J = 12, 6.5, 1 Hz, 1).

Anal. Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.90; H, 6.21; N, 5.07.

3,5-Dihydro-5,9b-*o*-benzenobenz[*e*]isoindol-1(2*H*)-one (4a). From 13.68 g of 9-anthroyl chloride and 10 g of propargylamine there was obtained 14.54 g of crude *N*-propargyl-9-anthramide as a solid. An analytical sample (ethanol) had the following: mp 201–202 °C; NMR τ 1.5–2.8 (m, 9), 3.7 (br, 1), 5.7 (dd, 2), 7.7 (t, J = 2.5 Hz, 1).

Anal. Calcd for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.50; H, 5.08; N, 5.29.

A mixture of 10 g of crude *N*-propargyl-9-anthramide and 200 mL of *p*-xylene was heated under reflux overnight. The solvent was removed, and the residue was sublimed at a 200–210 °C bath temperature (0.5 μm). Crystallization of the sublimate from 110 mL of acetonitrile gave 4.7 g (47%) of **4a**, mp 264–265 °C, unchanged on recrystallization: NMR τ 2.3–3.3 (m, 10), 4.8 (d, J = 6 Hz, 1), 5.9 (d, J = 2 Hz, 2).

Anal. Calcd for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.19; H, 5.11; N, 5.40.

2-Methyl-3,5-dihydro-5,9b-*o*-benzenobenz[*e*]isoindol-1-(2*H*)-one (4b). From 20.8 g of 9-anthroyl chloride and 14.23 g of *N*-methylpropargylamine there was obtained 23.3 g of the crude *N*-methyl-*N*-propargyl-9-anthramide as an oil: NMR τ 1.7–2.9 (m, 9), 5.4 (d, J = 2.5 Hz, 1.3), 6.4 (d, J = 2.5 Hz, 0.7), 6.7 (s, 0.9), 7.4 (s, 2.1), 7.7 (t, J = 2.5 Hz, 0.7), 8.0 (t, 0.3). The spectrum shows the presence of two rotamers.

A mixture of 23.3 g of crude *N*-methyl-*N*-propargyl-9-anthramide and 200 mL of toluene was heated under reflux for 4 h. The solvent was removed, and the residue was crystallized from 300 mL of acetonitrile to give 16.4 g (70%) of **4b**, mp 250–255 °C. An analytical sample had the following: 250–255 °C; NMR τ 2.3–3.3 (m, 9), 4.8 (d, J = 6 Hz, 1), 5.9 (d, J = 2 Hz, 2), 6.9 (s, 3).

(13) This fact has been noted by others: cf. H. W. Gschwend, A. O. Lee, and H.-P. Meier, *J. Org. Chem.*, **38**, 2169 (1973).

(14) J. S. Meek, P. A. Monroe, and C. J. Bourboulis, *J. Org. Chem.*, **28**, 2572 (1963), and references cited therein; P. V. Alston, R. M. Ottenbrite, and J. Newly, *ibid.*, **44**, 4939 (1979); cf. also ref 12.

(15) For other determinations of the thermodynamic parameters of intramolecular Diels–Alder reactions, see: H. W. Gschwend and H. P. Meier, *Angew. Chem., Int. Ed. Engl.*, **11**, 294 (1972); ref 13.

Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.84; H, 5.66; N, 5.10.

Kinetic Runs. One-percent solutions of *N*-methyl-*N*-propargyl-9-anthramide in benzene (bp 80.5 °C), 1:1 toluene–benzene (bp 91.6 °C), 9:2 toluene–benzene (bp 100.1 °C), and toluene (bp 111.3 °C) were heated under reflux, and samples were removed at intervals; the solvents were removed, and the residues were analyzed by NMR spectroscopy. The ratios of unreacted starting material to product were determined by integration and by cutting and weighing the expanded traces of the *N*-methyl signals. The temperatures were measured with a calibrated thermometer immersed in the liquid. The first-order rate constants (s^{-1}, obtained by the least-squares method) were 2.72×10^{-5} at 80.5 °C, 7.07×10^{-5} at 91.6 °C, 1.79×10^{-4} at 100.1 °C, and 3.93×10^{-4} at 111.3 °C.

9-Anthraceneacetic Acid. A solution of 30 g of sodium borohydride in a mixture of 400 mL of methanol and 100 mL of water was added, during 30 min, to a slurry of 200 g of 9-anthraldehyde in 1 L of methanol. The temperature rose to 50 °C. The mixture was stirred at room temperature for 1.5 h, ice and water (ca. 1 L) were added, and the precipitate was collected, washed twice with water, and dried. The 9-anthracenemethanol so obtained was heated under reflux with 80 mL of thionyl chloride in 2000 mL of benzene for 3 h. The solid obtained on removal of the benzene (9-(chloromethyl)anthracene) was dissolved in 1500 mL of dimethyl sulfoxide, the solution was heated to 60 °C, and a solution of 90 g of potassium cyanide in 200 mL of water was added during 30 min, keeping the temperature at 60 °C (external cooling). Stirring at 60 °C was continued for 1 h. After the mixture was allowed to stand at room temperature overnight, 4 L of water was added, and the precipitate was washed with water and dried to give 189 g of crude 9-anthraceneacetonitrile. A mixture of 116 g of this product, 50 g of sodium hydroxide, and 350 mL of Cellosolve was heated under reflux for 2 h. The mixture was cooled, diluted with water, and acidified. The crude acid was collected by filtration, washed with water, and dissolved in a boiling solution of 60 g of sodium carbonate in 2 L of water. The mixture was cooled to 60 °C and filtered. The filtrate was cooled and acidified to give 102 g of 9-anthraceneacetic acid which was used without any further purification.

1,9-Dihydro-2*H*-4a,9-*o*-benzenobenz[*f*]isoquinolin-3-(4*H*)-one (5a). A mixture of 8.6 g of 9-anthraceneacetic acid and 20 mL of thionyl chloride was stirred at room temperature for 1 h. The excess reagent was removed under vacuum, the residue was dissolved in toluene, and the solvent was removed under vacuum. The residue (crude 9-anthraceneacetyl chloride) was dissolved in dry THF and added dropwise to a solution of 5 g of propargylamine in THF. The mixture was then stirred at 35–40 °C for 1 h, and the solvent was removed. The residual solid was washed with 15% sodium hydroxide solution and water and dried to give 8.9 g of crude *N*-propargyl-9-anthraceneacetamide. A mixture of 40.5 g of the amide and 200 mL of toluene, contained in four evacuated and sealed Carius tubes, was heated to 190 °C for 16 h. Removal of the solvent gave crude **5a**. A sample was crystallized from dimethylformamide: mp 254–256 °C; NMR [in $(CD_3)_2SO$] τ 2.3–3.5 (m, 10), 4.9 (d, J = 6 Hz, 1), 6.3 (m, 2), 6.7 (s, 2).

Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.14; H, 5.52; N, 5.28.

2-Methyl-1,9-dihydro-2*H*-4a,9-*o*-benzenobenz[*f*]isoquinolin-3(4*H*)-one (5b). From 23.19 g of anthraceneacetic acid and 15 g of *N*-methylpropargylamine there was obtained 25.52 g of crude *N*-methyl-*N*-propargyl-9-anthraceneacetamide: NMR τ 1.6–2.7 (m, 9), 5.5–6.0 (br s, and m, 4), 6.8–7.1 (2 br s, 3), 7.5–7.8 (m, 1); the spectrum indicates the presence of two rotamers in solution. A mixture of 24.71 g of the amide and 120 mL of *p*-xylene was heated under reflux for 3.25 h. The precipitate obtained on cooling was washed with benzene and dried to give 20.52 g (83%) of **5b**, mp 261–263 °C dec. An analytical sample (dichloroethane) had the following: mp 261–263 °C; NMR τ 2.6–3.3 (m, 9), 4.9 (d, J = 6 Hz, 1), 6.0 (d, J = 2 Hz, 2), 6.4 (s, 2), 7.1 (s, 3).

Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.88. Found: C, 83.49; H, 6.01; N, 4.73.

3-Methyl-1,2,3,10-tetrahydro-5a,10-*o*-benzenonaphth[1,2-*d*]azepin-4(5*H*)-one (6). From 17.0 g of 9-anthraceneacetic acid and 12.9 g of 3-butynylamine there was obtained, after crystallization from ethanol, 15.5 g of *N*-methyl-*N*-(3-butynyl)-9-anthraceneacetamide. A mixture of 12 g of this product and 120 mL of toluene, contained in three Carius tubes, was deoxygenated (one freeze–thaw cycle), and the tubes were sealed under vacuum and heated to 220 °C for 36 h. Removal of the solvent and crystallization of the residue from 250 mL of acetonitrile gave 7.16 g (60%) of **6**. An analytical sample had the following: mp 256–258 °C; NMR τ 2.5–3.4 (m, 9), 5.0 (d, J = 6 Hz, 1), 6.1 (s, 2), 6.7–7.5 (s and m, 7).

Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 84.14; H, 6.43; N, 4.89.

5,6,6a,6b,7,8,9,10-Octahydro-12*H*-5,12a-*o*-benzenobenz[*e*]pyrido[2,1-*a*]isoindol-12-one (7). A solution of 6.2 g of 9-anthroyl chloride in 20 mL of tetrahydrofuran was added slowly to a stirred mixture of 3.36 g of 2-vinylpiperidine, 3.7 g of magnesium oxide, and 30 mL of tetrahydrofuran. After being stirred overnight, the mixture was filtered, the filtrate was concentrated, and the residue was heated under reflux with 100 mL of *p*-xylene for 20 h. Removal of the solvent and crystallization of the residue from acetonitrile gave 2.36 g (29%) of **7**, mp 224–225 °C. A small sample was purified further by chromatography on Florisil (elution with 5/95 THF/methylene chloride) and crystallization from acetonitrile: mp 224–225 °C; NMR τ 1.9–2.9 (m, 8), 5.3–5.7 (m, 2), 7.0–9.2 (m, 10).

Anal. Calcd for $C_{22}H_{21}NO$: C, 83.77; H, 6.71; N, 4.44. Found: C, 84.15; H, 6.66; N, 4.48.

3,3a,4,5-Tetrahydro-5,9b-*o*-benzenobenz[*e*]isoindole (8a). The following procedure illustrates the synthesis of the cyclic imines in Scheme II. A mixture of 24.7 g of 9-anthraldehyde,[8] 35 mL of allylamine, and 70 mL of ethanol was heated under reflux for 1 h. The solvent was removed, and the residue was crystallized from 50 mL of isopropyl alcohol to give 25.4 g (87%) of *N*-allyl-9-anthracenemethanimine, mp 72.5–73.5 °C. An analytical sample had the following: mp 72.5–73.5 °C; NMR τ 1.0 (t, J = 1 Hz, 1), 1.7–2.9 (m, 9), 3.2–4.1 (m, 1), 4.4–5.0 (m, 2), 5.3–5.5 (d, split further, 2).

Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.13; H, 6.33; N, 5.66.

A mixture of 25.0 g of *N*-allyl-9-anthracenemethanimine and 300 mL of *p*-xylene was heated under reflux for 24 h. Removal of the solvent and crystallization of the residue from 70 mL of benzene gave 21.2 g (85%) **8a**, mp 120–121 °C. An analytical sample had the following: mp 120.5–121 °C; NMR τ 1.1 (dd, J = 3, 1 Hz, 1), 2.5–3.1 (m, 8), 5.6 (dd, J = 3.5, 1 Hz, 1), 5.9 (ddd, J = 14.5, 6.5, 1 Hz, 1), 7.2 (ddd, J = 14.5, 11, 3 Hz, 1), 7.9 (m, 1), 8.1 (ddd, J = 11.5, 9.5, 3.5 Hz, 1), 8.6 (ddd, J = 11.5, 7.5, 1 Hz, 1).

Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.01; H, 6.28; N, 5.51.

2-(Trifluoroacetyl)-1,2,3,3a,4,5-hexahydro-5,9b-*o*-benzenobenz[*e*]isoindol-1-ol (9b). To 30 g of *N*-allyl-9-anthracenemethanimine in 100 mL of methylene chloride was added slowly 30 g of trifluoroacetic anhydride. The temperature rose to 39 °C. The mixture was concentrated after 24 h at room temperature, and the residue was stirred with 200 mL of methylene chloride and 100 mL of 15% aqueous sodium hydroxide solution for 1 h. From the dried methylene chloride layer there was obtained 32.1 g of an oil, the NMR spectrum of which showed the presence of 25% of 9-anthraldehyde, 8% of unreacted starting material, and 67% of **9b**. Crystallization from 100 mL of 1,2-dichloroethane gave 10.9 g (25%) of **9b**, mp 155–166 °C. An analytical sample had the following: mp 166–171 °C; ^{19}F NMR narrow ($W_{1/2}$ < 2 Hz) multiplets at −70.73 and −73.78 ppm from $CFCl_3$ in a ratio of 16:84. Melting point and NMR indicate the presence of two isomers (presumably OH at C-1 which is exo and endo with respect to the bridge).

Anal. Calcd for $C_{20}H_{16}F_3NO_2$: C, 66.85; H, 4.49; N, 3.90. Found: C, 66.84; H, 4.68; N, 3.74.

When **9b** was heated under reflux with 10% alcoholic KOH, **8a** was obtained in essentially quantitative yield.

5-Chloro-3,3a,4,5-tetrahydro-*o*-benzenobenz[*e*]isoindole (8b). From 10.96 g of 10-chloro-9-anthraldehyde and 15 mL of allylamine there was obtained 11.68 g (92%) of *N*-allyl-10-

chloro-9-anthracenemethanimine, mp 113–114 °C. An analytical sample had the following: 113.5–114.5 °C; NMR τ 0.7 (t, 1), 1.6–2.7 (m, 8), 3.3–4.0 (m, 1), 4.2–4.7 (m, 2), 5.2 (d, 2).

Anal. Calcd for $C_{18}H_{14}ClN$: C, 77.27; H, 5.04; N, 5.00. Found: C, 77.24; H, 5.10; N, 4.91.

A mixture of 4.51 g of *N*-allyl-10-chloro-9-anthracenemethanimine and 20 mL of *p*-xylene was heated under reflux for 3.5 h. The solvent was removed, and the crude **8b** was reduced and methylated with formaldehyde and formic acid as described for the preparation of **13c**. The yield of 5-chloro-2-methyl-1,2,3,3a,4,5-hexahydro-5,9b-*o*-benzenobenz[*e*]isoindole after one crystallization from acetonitrile was 1.63 g (mp 125–126 °C). An analytical sample had the following: mp 125–126 °C; NMR τ 2.1–3.0 (m, 8), 6.0 and 6.5 (AB q, J = 10 Hz, 2), 7.3 (s, 3), 7.0–8.3 (m, 5).

Anal. Calcd for $C_{19}H_{18}ClN$: C, 77.14; H, 6.13; N, 4.73. Found: C, 77.51; H, 5.98; N, 4.91.

3,5-Dihydro-5,9b-*o*-benzenobenz[*e*]isoindole (10a). From 16.7 g of 9-anthraldehyde[8] and 5 g of propargylamine there was obtained, after crystallization from 100 mL of acetonitrile, 16.1 g (82%) of *N*-propargyl-9-anthracenemethanimine, mp 143–144 °C. An analytical sample had the following: mp 143–144 °C; NMR τ 0.2 (t, J = 2 Hz, 1), 1.7–3.0 (m, 9), 5.1 (t, J = 2 Hz, 2), 7.3 (t, J = 2 Hz, 1).

Anal. Calcd for $C_{18}H_{13}N$: C, 88.86; H, 5.39; N, 5.76. Found: C, 88.83; H, 5.56; N, 5.87.

A mixture of 19.4 g of crude *N*-propargyl-9-anthracenemethanimine and 200 mL of *p*-xylene was heated under reflux for 3 h. As the mixture cooled, 14.6 g of **10a** (mp 212–214 °C) precipitated. Another 1.4 g of product was obtained by removing the solvent from the mother liquor and crystallizing the residue from 50 mL of acetonitrile (combined yield 82%). An analytical sample had the following: mp 212–214 °C; NMR τ 1.1 (m, 1), 2.5–3.5 (m, 9), 4.3 (d, J = 6 Hz, 1), 5.4 (t, J = 2 Hz, 2).

Anal. Calcd for $C_{18}H_{13}N$: C, 88.86; H, 5.39; N, 5.76. Found: C, 89.10; H, 5.58; N, 5.66.

4,6-Dihydro-3*H*-6,10b-*o*-benzenobenz[*h*]isoquinoline (10b). *N*-(3-butynyl)-9-anthracenemethanimine, obtained from 5.00 g of 9-anthraldehyde[8] and 1.97 g of 3-butynylamine, was used without further purification: NMR τ 0.8 (t, J = 1 Hz, 1), 1.5–2.9 (m, 9), 6.2 (5, J = 7 Hz, split further, 2), 7.3 (dd, J = 7, 2.5 Hz, 2), 8.0 (t, J = 2.5 Hz, 1). A mixture of 5 g of the imine and 50 mL of toluene, contained in a sealed Carius tube, was heated to 200 °C for 24 h. The product was sublimed at a 150–160 °C bath temperature (1 μm), and the sublimate was crystallized from isopropyl alcohol to give 2.10 g of **10b**, mp 165–167 °C. An analytical sample had the following: mp 166–167 °C; NMR τ 0.9 (t, 1), 2.3–3.0 (m, 8), 3.2 (dt, J = 6, 2 Hz, 1), 4.8 (d, J = 6 Hz, 1), 6.0–6.3 (m, 2), 7.4–7.7 (dt, J = 6, 2 Hz, 2).

Anal. Calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.31; H, 6.07; N, 5.25.

3,4,5,6,6a,7-Hexahydro-1*H*-7,11b-*o*-benzenobenzo[*e*]cyclopent[*h*]isoindole (11) and 2-Methyl-1,3,4,5,6,6a-hexahydro-7*H*-7,11b-*o*-benzenobenzo[*e*]cyclopent[*h*]isoindole. *N*-(1-Cyclopentenylmethyl)-9-anthracenemethanimine was obtained in 64% yield, mp 60–62 °C (isopropyl alcohol), by heating 8.56 g of 9-anthraldehyde,[8] 4.64 g of 1-cyclopentenylmethanamine, and 20 mL of ethanol under reflux for 4.5 h. An analytical sample had the following: mp 64–65 °C; NMR τ 0.9 (narrow t, 1), 1.5–3.0 (m, 9), 4.4 (m, 1), 5.7 (narrow t, 2), 7.5–6.1 (m, 6).

Anal. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91. Found: C, 88.52; H, 6.84; N, 4.80.

A mixture of 4.85 g of *N*-(1-cyclopentenylmethyl)-9-anthracenemethanimine and 30 mL of toluene, contained in an evacuated and sealed Carius tube, was heated to 200 °C for 12 h. Removal of the solvent gave crude **11** as an oil that slowly solidified: NMR τ 1.2 (dd, J = 1.5, 3 Hz, 1), 2.6–3.2 (m, 8), 6.0 (d, J = 2 Hz, 1), 6.2 (dd, J = 13, 1.5, 3 Hz, 1), 7.1 (d, J = 13 Hz, split further, 1), 7.6–9.6 (m, 7). The crude product was heated under reflux with 50 mL of formic acid and 20 mL of 37% aqueous formaldehyde solution for 3 h. Concentrated hydrochloric acid (5 mL) was added, the mixture was concentrated to dryness, and the residue was made basic and extracted with methylene chloride. Removal of the solvent from the dried extracts gave 4.60 g of crude 2-methyl-1,3,4,5,6,6a-hexahydro-7*H*-7,11b-*o*-benzenobenz[*e*]-cyclopent[*h*]isoindole which was converted to the hydrochloride (4.00 g) with gaseous hydrogen chloride in ether. Crystallization from 20 mL of isopropyl alcohol gave 2.57 g of purified product, mp 284 °C dec. An analytical sample had a melting point of 284 °C dec.

Anal. Calcd for $C_{22}H_{24}ClN$: C, 78.20; H, 7.16; N, 4.14. Found: C, 77.72; H, 6.97; N, 4.12.

Spiro[5*H*-5,9b-*o*-benzenobenz[*e*]isoindole-3,1′-cyclohexane] (12). *N*-(1-Ethynylcyclohexyl)-9-anthracenemethanimine was obtained by heating a mixture of 49 g of 9-anthraldehyde,[8] 51 g of 1-ethynylcyclohexylamine and 100 mL of ethanol under reflux for 24 h. Removal of the solvent and crystallization of the residue from isopropyl alcohol (230 mL) gave 54.5 g (74%) of the imine, mp 115–117 °C. An analytical sample had the following: mp 118–120 °C; NMR τ 0.2 (s, 1), 1.5–3.0 (m, 9), 7.1 (s, 1), 7.8–9.2 (m, 10).

Anal. Calcd for $C_{23}H_{21}N$: C, 88.70; H, 6.80; N, 4.50. Found: C, 88.67; H, 6.80; N, 4.34.

A mixture of 40.0 g of *N*-(1-ethynylcyclohexyl)-9-anthracenemethanimine and 400 mL of *p*-xylene was heated under reflux for 3 h. Removal of the solvent and crystallization of the residue from 200 mL of ethyl acetate gave 23.5 g of **12** as a colorless solid, mp 190–191 °C. A second crop (10.1 g) was obtained from the mother liquors (combined yield 33.6 g, 84%). An analytical sample had the following: mp 190–191 °C; NMR τ 1.0 (s, 1), 2.5–3.3 (m, 9), 4.7 (d, J = 5.5 Hz, 1), 7.9–8.9 (m, 10).

Anal. Calcd for $C_{23}H_{21}N$: C, 88.70; H, 6.80; N, 4.50. Found: C, 88.77; H, 6.58; N, 4.25.

2-Benzyl-1,2,3,5-tetrahydro-5,9b-*o*-benzenobenz[*e*]isoindole (13a). A mixture of 100 g of 9-anthraldehyde,[8] 53 g of benzylamine, and 300 mL of ethanol was heated under reflux under nitrogen for 2.5 h. The solution of *N*-benzyl-9-anthracenemethanimine so obtained was cooled to 60 °C, and 18.78 g of sodium borohydride was added slowly, keeping the temperature at 60–65 °C. After the mixture was stirred at room temperature overnight, the excess hydride was destroyed by the slow addition of concentrated hydrochloric acid. The mixture was then made basic and extracted several times with methylene chloride. Removal of the solvent from the dried extracts gave 139.9 g of *N*-benzyl-9-anthracenemethanamine: NMR τ 1.8–3.0 (m, 14), 5.5 (s, 2), 6.2 (s, 2), 8.5 (s, 1). The product was dissolved in 300 mL of methylene chloride, 200 mL of 15% aqueous sodium hydroxide solution and 100 mL of propargyl bromide were added, and the mixture was stirred vigorously under nitrogen at room temperature for 3 h. The layers were separated, the aqueous layer was extracted once with methylene chloride, and the combined extracts were washed with concentrated sodium chloride solution and dried. Removal of the solvent gave 153.5 g of crude *N*-benzyl-*N*-propargyl-9-anthracenemethanamine: NMR τ 1.5–3.0 (m, 14), 5.5 (s, 2), 6.3 (s, 2), 6.9 (d, J = 2.5 Hz, 2), 7.7 (t, J = 2.5 Hz, 1). The amine was dissolved in 1000 mL of toluene, and the solution was heated under reflux for 2.2 h. Removal of the solvent from the filtered mixture and crystallization of the residue from isopropyl alcohol gave 124.2 g (76%) of **13a**: mp 125–126 °C; NMR τ 2.4–3.6 (m, 14), 5.0 (d, J = 6 Hz, 1), 6.2 (s, 2), 6.3 (s, 2), 6.7 (d, J = 2 Hz, 2).

Anal. Calcd for $C_{25}H_{21}N$: C, 89.51; H, 6.31; N, 4.18. Found: C, 89.77; H, 6.26; N, 4.24.

1,2,3,5-Tetrahydro-5,9b-*o*-benzenobenz[*e*]isoindole (13b). To a slurry of 10.19 g of **10a** in 50 mL of methanol and 10 mL of acetic acid was added slowly, with cooling, 4.70 g of sodium cyanoborohydride. The mixture was stirred at room temperature overnight, the excess hydride was destroyed with concentrated hydrochloric acid (ice bath), and the mixture was made basic and extracted with methylene chloride. Removal of the solvent from the dried extract gave 10.49 g of crude **13b** as an oil: NMR τ 2.6–3.7 (m, 9), 4.9 (d, J = 6 Hz, 1), 6.0 (s, 2), 6.5 (d, J = 2 Hz, 2), 7.5 (s, 1). The hydrochloride melted at 273 °C (dec) after crystallization from isopropyl alcohol.

Anal. Calcd for $C_{18}H_{16}ClN$: C, 76.73; H, 5.72; N, 4,97. Found: C, 76.62; H, 5.88; N, 4.93.

2-Methyl-1,2,3,5-tetrahydro-5,9b-*o*-benzenobenz[*e*]isoindole (13c). A mixture of 8.19 g of **10a**, 25 mL of formic acid, and 25 mL of aqueous formaldehyde solution was heated under reflux for 3 h. Concentrated hydrochloric acid (10 mL) was added, and the volatiles were removed. The residue was stirred with aqueous sodium hydroxide solution and methylene chloride.

Removal of the solvent from the dried methylene chloride extracts and crystallization of the residue from acetonitrile gave, in two crops, 5.04 g (58%) of **13c**, mp 196–197 °C. An analytical sample had the following: mp 196–197 °C; NMR 2.4–3.1 (m, 8), 3.3 (dt, J = 6, 2 Hz, 1), 4.8 (d, J = 6 Hz, 1), 6.1 (s, 2), 6.6 (d, J = 2 Hz, 2), 7.3 (s, 3).

Anal. Calcd for $C_{19}H_{17}H$: C, 87.99; H, 6.61; N, 5.40. Found: C, 88.05; H, 6.91; N, 5.32.

2-Allyl-1,2,3,5-tetrahydro-5,9b-*o*-benzenobenz[*e*]isoindole (14) and 2-Propargyl-1,2,3,3a,4,5-hexahydro-5,9b-*o*-benzenobenz[*e*]isoindole (15). *N*-Allyl-*N*-propargyl-9-anthracenemethanamine was prepared from 9-anthraldehyde and allylamine followed by reduction and alkylation with propargyl bromide as described for the synthesis of **13a** above. A solution of this product in toluene was heated under reflux for 2.2 h. The NMR spectrum of the crude mixture obtained after removal of the solvent showed the presence of **14** (75%) and **15** (25%). For **14**: NMR τ 2.5–3.1 (m, 8), 3.5 (dt, J = 6, 2 Hz, 1), 3.7–4.8 (m, 3), 5.0 (d, J = 6 Hz, 1), 6.2 (s, 2), 6.7 (d, J = 7 Hz, and d, J = 2 Hz, 4). For **15**: NMR τ 2.5–3.1 (m, 8), 5.8 (narrow m, 1), 6.1 and 6.6 (AB q, J = 12 Hz, 2), 6.5 (d, J = 2.5 Hz, 2), 7.1–9.2 (m, 5).

6a,7,10,11,12,12a-Hexahydro-5,12b-*o*-benzeno-9*H*-naphth[1,2-*a*]indolizine (17). A mixture of 10.0 g of 2-(9-anthryl)-pyridine,[9] 35 mL of propargyl bromide and 50 mL of methylene chloride was allowed to stand at room temperature for 16 h. The solvent and excess bromide were removed, and the residue was dissolved in a mixture of 100 mL of methanol and 15 mL of acetic acid. Sodium cyanoborohydride (7.2 g) was added with cooling, and the mixture was stirred at room temperature for 6 h. The excess hydride was destroyed by addition of 50 mL of concentrated hydrochloric acid to the cooled mixture. After being stirred at room temperature for 1 h, the mixture was made basic and extracted with methylene chloride. The product so obtained was dissolved in 50 mL of methanol, 25 mL of concentrated hydrochloric acid was added, and the mixture was allowed to stand at room temperature for 24 h. The product obtained after basic workup was chromatographed on Florisil, and the fraction eluted with methylene chloride was crystallized from acetonitrile to give 3.98 g (34%) of **17** in two crops; mp 204–206 °C. An analytical sample had the following: mp 205–206 °C; NMR τ 2.0–3.5 (m, 9), 5.0 (d, J = 6 Hz, 1), 6.0–9.0 (m, 11).

Anal. Calcd for $C_{22}H_{21}N$: C, 88.25; H, 7.07; N, 4.68. Found: C, 87.91; H, 7.12; N, 5.00.

2-Methyl-1,2,3,3a,4,5-Hexahydro-5,9b-*o*-benzenobenz[*e*]-isoindole-1-carbonitrile (18). To a mixture of 20 g of 9-anthraldehyde,[8] *N*-methylallylamine hydrochloride (prepared from 12 g of *N*-methylallylamine in ether with gaseous hydrogen chloride) and 70 mL of dioxane was added, with cooling, a solution of 4.6 g of sodium cyanide in 35 mL of water. After being stirred at room temperature for 3 days, the mixture was made basic and extracted with methylene chloride. The residue left after removal of the solvent from the dried extracts was stirred with 200 mL of ether, and hydrogen chloride was passed into the filtered solution. The hydrochloride was collected and reconverted to the crude free base, α-(*N*-methylallylamino)-9-anthraceneacetonitrile, to yield 5.3 g of a tan solid. The crude product was heated under reflux with 100 mL of *p*-xylene for 5 h. As the mixture cooled, 1.63 g of **18**, mp 209–212 °C, precipitated. An analytical sample had the following: mp 209–211 °C; NMR τ 1.9–3.2 (m, 8), 5.7–5.9 (s and t, 2), 7.3–9.1 (s and m, 8).

Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.60; H, 6.42; N, 9.77.

3,5-Dihydro-1*H*-5,9b-*o*-benzenonaphtho[1,2-*c*]furan (19). A mixture of 2.50 g of 50% sodium hydride in oil (previously washed with hexane), 10.20 g of 9-anthracenemethanol, and 100 mL of THF was stirred at room temperature for 1 h and then heated under reflux for 1 h. The mixture was cooled, and a solution of 7.04 g of propargyl bromide in 10 mL of THF was added slowly. After being heated under reflux for 2 h, the cooled mixture was treated with water, and the product was extracted with ether to give 10.3 g of crude 9-anthracenemethyl propargyl ether: NMR τ 1.2–2.6 (m, 9), 4.2 (s, 2), 5.5 (d, J = 2.5 Hz, 2), 7.2 (t, J = 2.5 Hz, 1), in addition to weak bands in the aromatic region. The crude product was used without further purification.

A mixture of 10.1 g of the crude ether and 100 mL of *p*-xylene was heated under reflux for 3 h. As the mixture cooled, 6.82 g (68%) of **19**, mp 200–201.5 °C, precipitated. An analytical sample (MeCN) had the following: mp 200.5–201.5 °C; NMR τ 2.6–3.2 (m, 8), 4.5 (dt, J = 2.5, 6 Hz, 1), 5.9 (d, J = 6 Hz, 1), 6.1 (s, 2), 6.7 (d, J = 2.5 Hz, 2).

Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.67; H, 5.61.

9-Anthracenemethanethiol. To a solution of 64 g of 9-(chloromethyl)anthracene in 200 mL of dimethylformamide, kept at 50 °C under nitrogen, was added a solution of 40 g of thiourea in 120 mL of dimethylformamide, and the mixture was slowly (during the course of 1 h) warmed to 80 °C. After 30 min at that temperature, a precipitate formed which was collected after cooling of the mixture, washed with dimethylformamide and ether, and dried to give 31.7 g of crude (9-anthracenemethyl)thiouronium chloride, mp 233–234 °C. Another 40.1 g of less pure product was obtained from the filtrate by addition of 500 mL of ether; it was suitable for conversion to the methanethiol without further purification. A mixture of 20.05 g of the thiouronium salt, 60 mL of a 15% aqueous sodium hydroxide solution, and 150 mL of ethanol was heated under reflux *under nitrogen* for 10 min. The cooled mixture was filtered under nitrogen pressure, and the filtrate was acidified, still under nitrogen, with a mixture of 30 mL of concentrated hydrochloric acid and 100 mL of water. At this point a nitrogen atmosphere was no longer required. The product was collected by filtration, washed with water, and dissolved on the filter in methylene chloride. The dried organic layer was concentrated, and the residue was crystallized from 100 mL of acetonitrile to give 12.00 g of product, mp 141–142 °C. An analytic sample had the following: mp 141–142 °C; NMR τ 1.7–2.8 (m, 9), 5.4 (d, J = 7 Hz, 2), 8.1 (t, J = 7 Hz, 1).

Anal. Calcd for $C_{15}H_{12}S$: C, 80.31; H, 5.39; S, 14.30. Found: C, 79.98; H, 5.49; S, 14.11.

9-Anthracenemethyl Propargyl Sulfide. The second crop of thiouronium salt (see above) was converted to 9-anthracenemethanethiol as described above. The product was dissolved in 300 mL of methylene chloride and treated, under nitrogen, with excess 15% aqueous sodium hydroxide solution. The thick precipitate was stirred by hand, collected by filtration, and washed once with methylene chloride. The sodium salt was then stirred under nitrogen with 50 mL of 15% aqueous sodium hydroxide solution, 200 mL of water, 200 mL of methylene chloride, and 25 mL of propargyl bromide at room temperature for 1 h. The organic layer, on evaporation of the solvent, gave 21.6 g of product as a solid, mp 99–100 °C, after crystallization from acetonitrile: NMR τ 1.6–2.8 (m, 9), 5.3 (s, 2), 6.8 (d, J = 2.5 Hz, 2), 7.7 (t, J = 2.5 Hz, 1).

Anal. Calcd for $C_{18}H_{14}S$: C, 83.17; H, 5.14; S, 11.69. Found: C, 82.66; H, 5.48; S, 11.78.

3,5-Dihydro-1*H*-5,9b-*o*-benzenonaphtho[1,2-*c*]thiophene (20). A mixture of 18.2 g of crude 9-anthracenemethyl propargyl sulfide and 150 mL of *p*-xylene was heated under reflux for 3.3 h. Removal of the solvent and crystallization of the residue from 50 mL of acetonitrile gave 13.5 g (74%) of **20**, mp 159–160 °C. An analytical sample had the following: mp 159–160 °C; NMR τ 2.7–3.2 (m, 8), 3.5 (dt, J = 6, 2 Hz, 1), 5.0 (d, J = 6 Hz, 1), 6.1 (s, 2), 6.5 (d, J = 2 Hz, 2).

Anal. Calcd for $C_{18}H_{14}S$: C, 82.40; H, 5.38; S, 12.22. Found: C, 82.56; H, 5.48; S, 12.02.

Methyl 3-[2-(9-Anthryl)ethoxy]acrylate. A mixture of 5.4 g of 9-anthraceneethanol,[10] 20 mL of THF, 7 mL of methyl propiolate, and 0.3 g of *N*-methylmorpholine was stirred for 1 h. The temperature rose to 43 °C within 10 min. The solvent and excess reagent were removed, and the residue was crystallized from 20 mL of isopropyl alcohol to give 6.31 g (84% yield) of product, mp 91–92 °C, which was unchanged on further crystallization: NMR τ 1.5–2.8 (m, 10), 4.8 (d, J = 13 Hz, 1), 5.6–6.2 (m, 4), 6.3 (s, 3). The coupling constant indicates the product to be the trans isomer. There was no evidence for the presence of the cis isomer in the NMR spectrum of the mother liquors.

Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.46; H, 5.97.

Methyl 1,2,3a,4-Tetrahydro-5*H*-5,9b-*o*-benzenonaphtho[2,1-*b*]furan-4-carboxylate (21). A mixture of 6.00 g of methyl 3-[2-(9-anthryl)ethoxy]acrylate and 30 mL of toluene, contained in a sealed Carius tube, was heated to 185 °C for 24 h. Removal of the solvent gave a viscous oil which crystallized slowly.

Crystallization from isopropyl alcohol gave 4.72 g (79%) of **21**, mp 127–130 °C. An analytical sample had the following: mp 134–136 °C; NMR τ 2.3–2.8 (m, 8), 5.1 (d, J = 2 Hz, 1), 5.3–5.7 (dd, J = 9, 5 Hz, 2), 5.8 (d, J = 5 Hz, 1), 6.1 (s, 3), 6.7–7.2 (m, 3).

Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.15; H, 5.85.

3,5-Dihydro-5,9b-*o*-benzenonaphtho[1,2-*c*]furan-1-one (22). To a solution of 9-anthroyl chloride (prepared as described above from 50 g of 9-anthroic acid) in 100 mL of THF was added 100 mL of propargyl alcohol, keeping the temperature below 30 °C. The mixture was concentrated after 3 h, the residue was dissolved in 200 mL of methylene chloride, and the solution was washed with 5% sodium bicarbonate solution. Crystallization of the crude product from 100 mL of isopropyl alcohol gave 52 g (89%) of propargyl 9-anthroate: mp 90–92 °C; NMR τ 1.3–2.6 (m, 9), 4.6 (d, J = 2.5 Hz, 2), 7.2 (t, J = 2.5 Hz, 1).

Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.18; H, 4.66.

A solution of 43.0 g of the ester in 400 mL of *p*-xylene was heated under reflux (N_2) for 45 h. When the mixture cooled, 38.3 g (89%) of **22**, mp 263–264 °C, was obtained. A sample recrystallized from acetonitrile had the same melting point and the following NMR data: τ 2.3–3.2 (m, 9), 4.6 (d, J = 6 Hz, 1), 4.9 (d, J = 2 Hz, 2).

Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.92; H, 4.81.

1-(Propargyloxy)-3,5-dihydro-1*H*-5,9b-*o*-benzenonaphtho[1,2-*c*]furan (23). A mixture of 53.9 g of 9-anthraldehyde,[8] 3.5 g of *p*-toluenesulfonic acid, 500 mL of benzene, and 250 mL of propargyl alcohol was heated under reflux under a Soxhlet extractor containing 200 g of 4A molecular sieves for 20 h. The mixture was concentrated, and the residue was taken up in methylene chloride and washed with sodium bicarbonate solution. The solvent was removed from the dried solution, and the residue was heated with 200 mL of ethanol. The solid obtained on cooling was sublimed at a 160–170 °C bath temperature (0.5 μm), and the sublimate was crystallized from 100 mL of acetonitrile to give 24.2 g (31%) of **23**, mp 168–175 °C, contaminated with a small amount of anthracene (cf. ref 8). An analytical sample (toluene) had the following: mp 175–176 °C; NMR τ 2.0–3.5 (m, 10), 5.0 (d, J = 6 Hz, 1), 5.2–5.8 (m, 4), 7.5 (t, J = 2.5 Hz, 1).

Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.19; H, 5.76.

1,2,3,3a,4,5-Hexahydro-5,9b-*o*-benzenobenz[*e*]inden-1-ol (25a). To a Grignard reagent, prepared from 17.2 g of magnesium turnings and 100 g of 4-bromo-1-butene in 800 mL of ether, was added a solution of 125 g of 9-anthraldehyde[8] in 300 mL of THF, keeping the temperature below 15 °C. The mixture was then stirred at 40 °C for 30 min, cooled, and treated with concentrated ammonium chloride solution. The product was extracted with methylene chloride; removal of the solvent from the dried extracts gave 156.2 g of crude 1-(9-anthryl)-4-penten-1-ol contaminated by the reduction product, 9-anthracenemethanol, and some unreacted 9-anthraldehyde. It was dissolved in 700 mL of *p*-xylene, and the mixture was heated under reflux for 26 h. The precipitate (70 g) formed on cooling was heated under reflux with 200 mL of *p*-xylene and 23 g of maleic acid for 40 min. The mixture was allowed to cool to 80 °C, and 250 mL of 15% sodium hydroxide solution was added. When the solution was cooled with ice, a precipitate formed which was collected by filtration, washed with water and cold benzene, dried, and crystallized from 150 mL of isopropyl alcohol to give 31 g (20% yield) of **25a**: mp 166–167 °C; NMR τ 1.8–3.0 (m, 8), 4.8 (dt, J = 3, 9 Hz, 1), 5.7 (m, 1), 7.3–9.1 (m, 8).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.86; H, 7.08.

1,2,3,4,10,10a-Hexahydro-4a,9-*o*-benzenophenanthr-4-ol (25b). Crude 1-(9-anthryl)-5-hexen-1-ol (165.5 g), prepared as described above from 138 g of 9-anthraldehyde,[8] 100 g of 5-bromo-1-pentene, and 17 g of magnesium, was dissolved in 400 mL of *p*-xylene, and the mixture was heated under reflux for 17 h. Maleic anhydride (30 g) was added, and heating under reflux was continued for 45 min. The cooled mixture, after addition of 300 mL of 15% aqueous sodium hydroxide, was stirred for 1 h, and the precipitate was collected by filtration, washed with water and benzene, and dried to give 73.0 g (40% yield) of **25b**: mp 184–185 °C; NMR τ 2.0–3.0 (m, 8), 5.1–5.5 (m, 1), 5.9 (t, J = 2.5 Hz, 1), 7.5–9.5 (m, 10).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.84; H, 6.92.

3,3a,4,5-Tetrahydro-5,9b-*o*-benzenobenz[*e*]inden-1(2*H*)-one (26). To a solution of 30.1 g of 1,2,3,3a,4,5-hexahydro-5,9b-*o*-benzenobenz[*e*]inden-1-ol in 500 mL of acetone was added slowly, with cooling, a solution of 30 g of chromium trioxide in a mixture of 27 mL of sulfuric acid and 60 mL of water until the yellow color persisted. Only about one-third of the oxidant was used. After being stirred at room temperature for 30 min, the mixture was cooled, treated with aqueous sodium bisulfite solution, and extracted with methylene chloride. Removal of the solvent from the dried extracts and crystallization of the residue from 150 mL of acetonitrile gave 24.9 g of **26**, mp 178–179 °C. A second crop of 2.7 g was obtained from the mother liquors; combined yield 27.6 g (91%). An analytical sample had the following: mp 178–179 °C; NMR τ 2.2–2.5 (m, 1), 2.6–3.2 (m, 7), 5.7 (t, J = 2 Hz, 1), 7.2–9.5 (m, 7).

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.36; H, 6.09.

1,2,10,10a-Tetrahydro-4a,9-*o*-benzenophenanthr-4(3*H*)-one (27). 1,2,3,4,10,10a-hexahydro-4a,9-*o*-benzenobenzphenanthr-4-ol (59.7 g) was oxidized as described for the preparation of **26**. Crystallization of the crude product from 180 mL of *p*-xylene gave 48.4 g (82%) of **27**, mp 195–196 °C. An analytical sample had the following: mp 195–196 °C; NMR τ 1.5–1.8 (m, 1), 2.3–2.9 (m, 7), 5.5 (t, J = 2 Hz, 1), 6.7–9.2 (m, 10).

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.37; H, 6.83.

***N*-Methyl-3,3a,4,5-tetrahydro-5,9b-*o*-benzenobenz[*e*]-inden-1(2*H*)-imine (28).** A mixture of 10 g of **26**, 30 mL of ethanol, and 10 mL of methylamine, contained in an evacuated, sealed Carius tube, was heated to 170 °C for 15 h. Removal of the solvent gave 10.3 g of crude **28**. Crystallization of 3.7 g of the crude product from 10 mL of isopropyl alcohol gave 3.1 g of purified product, mp 138 °C. An analytical sample had the following: mp 138 °C; NMR τ 1.9–2.2 (m, 1), 2.6–3.1 (m, 7), 5.7 (t, 1), 6.5 (s, 3), 7.3–9.3 (m, 7).

Anal. Calcd for $C_{20}H_{19}N$: C, 87.87; H, 7.01; N, 5.12. Found: C, 88.27; H, 6.85; N, 5.01.

***N*-Methyl-1,2,10,10a-Tetrahydro-4a,9-*o*-benzenophenanthr-4-amine (29).** A mixture of 11.2 g of **27**, 25 mL of tetrahydrofuran, and 12 g of methylamine, contained in a sealed, evacuated Carius tube, was heated to 170 °C for 12 h. Removal of the solvent and crystallization of the residue from 75 mL of isopropyl alcohol gave 8.8 g (75%) of **29**, mp 130–131 °C, which was unchanged on further recrystallization: IR (KBr) 3400, 1640, (THF) 3390, 1655 cm^{-1}; NMR τ 1.9–3.2 (m, 8), 5.2 (t, J = 3.5 Hz, 0.8), 5.8 (m, 1), 6.5 (s, 0.3), 6.8–7.4 (m and s, 3.7), 7.6–9.2 (m, 7.1). The singlet at τ 6.5 presumably is due to the methyl group in the imine tautomer (cf. NMR of **28**); thus, in solution ($CDCl_3$), the equilibrium mixture consists of ca. 90% of **29** and 10% of its imine tautomer.

***N*-Methyl-*N*-propargyl-9-acridinecarboxamide (30).** A mixture of 8 g of 9-acridinecarboxylic acid[11] and 30 mL of thionyl chloride was heated under reflux for 4 h. Removal of excess reagent gave 8.6 g of crude 9-acridinecarbonyl chloride hydrochloride which was used without further purification. The acid chloride (4 g) was added slowly to a mixture of 4 mL of *N*-methylpropargylamine, 10 mL of triethylamine, and 20 mL of chloroform, keeping the temperature below 20 °C. Dilute sodium hydroxide solution was added after the mixture was stirred at room temperature overnight. The solid obtained from the organic layer (4 g) was crystallized from acetonitrile to give 2.60 g (66%) of **30**, mp 159–160 °C. An analytical sample had the following: mp 160–161 °C. The NMR shows two rotamers in a ratio of 45:55: τ 1.7–2.6 (m, 8), 5.3 (d, J = 2.5 Hz, 1.1), 6.2 (d, J = 2.5 Hz, 0.9), 6.5 (s, 1.35), 7.2 (s, 1.65), 7.5 (t, J = 2.5 Hz, 0.55), 7.7 (t, J = 2.5 Hz, 0.45).

Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.69; H, 5.26; N, 10.22.

2-Methyl-2,3-dihydro-1*H*-5,9b-*o*-benzeno-5*H*-pyrrolo[3,4-*c*]quinolin-1-one (31). A deoxygenated mixture of 2.06 g of **30** and 20 mL of toluene, contained in an evacuated (0.3 μm) sealed

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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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).

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