# Transannular Reactions in the Dibenzo[*a*,*d*]cycloheptene Series. V. Preparation of 10,11-Dihydro-5,10-(iminomethano)-5*H*-dibenzo[*a*,*d*]cycloheptenes

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Treatment of the ketonitrile **2***a* with sodium borohydride gave the lactone **3***a* which underwent ammonolysis to give 10,11-dihydro-5,10-(iminomethano)-5*H*-dibenzo[*a*,*d*]cyclohepten-13-one (**5***a*). This compound was used to prepare a number of 12- and 11,12-disubstituted derivatives of the ring system.

La réduction du céto-nitrile **2***a* par le borohydrure de sodium conduit à la lactone **3***a* qui, par ammonolyse, donne la dihydro-10,11 iminométhano-5,10 5*H*-dibenzo[*a*,*d*]cycloheptène-13 one (**5***a*). Ce composé a été utilisé pour préparer un certain nombre de dérivés substitués en -12 et -11,12 de ce système cyclique.

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We have previously (1) described the preparation of 10,11-dihydro-10,5-(iminomethano)-5*H*-dibenzo[*a*,*d*]cycloheptene derivatives. The pharmacological properties of these compounds were of sufficient interest to prompt us to prepare derivatives of the isomeric ring system **1**. Since previous work (2–4) has shown that suitably oriented substituents at positions 5 and 10 of the dibenzo[*a*,*d*]cycloheptene nucleus readily interact to form bridged systems, the same principle was adopted in the present case.

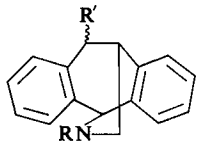
Treatment of the ketonitrile **2***a* with sodium borohydride followed by acid treatment resulted not only in reduction of the carbonyl group but also reduction of the 10,11- double bond and formation of the lactone **3***a*. A small amount of **3***a* was also obtained when the acid treatment was omitted. Nauta and his co-workers have recently reported that borohydride treatment of **2***a* gave a tetracyclic product (5). The reduction of the 10,11- double bond accords with the similar reduction of cinnamic acid esters (6). It is not clear whether the lactone **3***a* is formed via an iminolactone generated by an intramolecular Pinner reaction (7) or by prior hydration or hydrolysis of the nitrile function.

Support for the iminolactone pathway was obtained by converting **2***a* to the formamide **2***b* by the Leuckart reaction (8) and treating this product with sodium borohydride. The major product was the amidine **4**, precluding hydration or hydrolysis of the nitrile in this instance. A small amount of the lactam **5***a* was also obtained. On the other hand, treatment of the ketal **2***c* with sodium borohydride gave moderate amounts of the amide **6***a* and the acid **6***b* as well as the nitrile **6***c*. This ready hydration and hydrolysis of the 10-nitrile function contrasts markedly with the resistance of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5-nitrile to similar reaction conditions (9).

Ammonolysis of the lactone **3***a* proceeded normally, as with the structurally related 4-phenylisochromanone (10), giving a better route to the lactam **5***a*. In marked contrast, the isomeric lactone **7** decarboxylates under similar conditions (1). The substituted lactams **5***b*, *c* were prepared by using methylamine and ethylamine respectively in place of ammonium hydroxide. Reduction of **5***a–c* with lithium aluminum hydride gave the amines **1***a–c*. Similar reduction of the phenylacetyl derivative of **1***a* gave **1***d*.

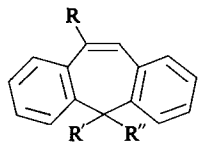
Several attempts were made to prepare 11-substituted derivatives of **1**. Despite the ready addition of hydride ion to **2***a*, attempts to add secondary amines were unsuccessful. Substituted acrylonitriles are known to be less reactive than acrylonitrile in cyanoethylation reactions (11). Bromination of **3***a* with *N*-bromosuccinimide gave the bromolactone **3***b*. Unfortunately this compound did not serve as a source for other 11-substituted lactones since treating it with dimethylamine gave the amide **2***d*. Similar bromination of the lactam **5***b* gave a mixture of two epimeric bromolactams **5***d*. They[1] were formed in approximately equal amounts but only one

[1]A referee has pointed out that the difference in chemical shifts of the C-11 protons in the isomers of A and B of **5***d* (see Experimental) is most probably due to the shielding effect of the amide carbonyl group. Isomer A will therefore be the *syn*-11-bromo compound (with respect to the amide bridge) and isomer B will be the *anti*-11-bromo compound.



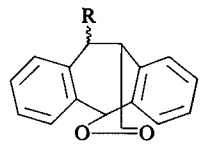
**1**

*a* R = R′ = H
*b* R = $CH_3$; R′ = H
*c* R = $C_2H_5$; R′ = H
*d* R = $CH_2CH_2C_6H_5$; R′ = H
*e* R = $CH_3$; R′ = $N(CH_2)_4$
*f* R = $CH_3$; R′ = $OCH_3$



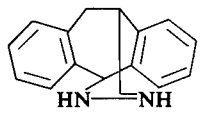
**2**

*a* R = CN; R′ + R″ = O=
*b* R = CN; R′ = NHCHO; R″ = H
*c* R = CN; R′ + R″ = $O(CH_2)_2O$
*d* R = $CON(CH_3)_2$; R′ = OH; R″ = H

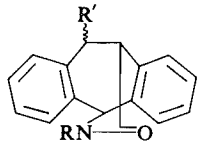


**3**

*a* R = H
*b* R = Br

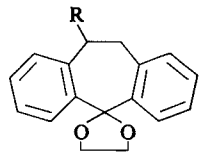


**4**



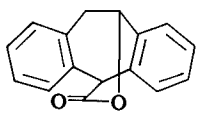
**5**

*a* R = R′ = H
*b* R = $CH_3$; R′ = H
*c* R = $C_2H_5$; R′ = H
*d* R = $CH_3$; R′ = Br
*e* R = $CH_3$; R′ = $N(CH_2)_4$
*f* R = $CH_3$; R′ = $OCH_3$

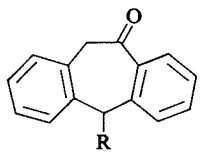


**6**

*a* R = $CONH_2$
*b* R = $CO_2H$
*c* R = CN

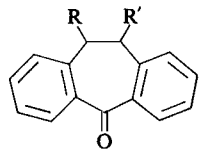


**7**



**8**

*a* R = $CONH_2$
*b* R = $CH_2NH_2$



**9**

*a* R = $CONH_2$; R′ = H
*b* R = $CH_2NH_2$; R′ = H
*c* R = CN; R′ = H
*d* R = $CH_2N(CH_3)_2$; R′ = H
*e* R = R′ = OH

epimer was readily isolated in a pure state. This compound readily underwent displacement reactions when it was treated with pyrrolidine and with sodium methoxide to give **5***e*, *f* respectively. Reduction of **5***e*, *f* with lithium aluminum hydride gave the amines **1***e*, *f*.

Since **8***a*, *b* are known to exist in the carbinolamine and carbinolamide forms (4), it was of interest to determine whether or not the isomeric **9***a*, *b* exhibited the same behavior. Deketalization of **6***a* gave the ketocarboxamide **9***a* and catalytic hydrogenation of **6***c* followed by deketalization gave the amino-ketone **9***b*. Methylation of **9***b* with formic acid – formaldehyde gave **9***d*. Spectral data indicated that **9***a*, *b*, *d* existed in the open form in neutral, acidic and basic media. In contrast, **9***e* is known to exist in the hemiketal form in alkaline media (2, 3), demonstrating that the 5-keto function is able to interact with bridge substituents in certain cases.

## Experimental

The n.m.r. spectra in the indicated solvents were determined using a Varian A-60A instrument; melting points were recorded on a Thomas-Hoover Uni-melt apparatus.

*5-Oxo-5H-Dibenzo[a,d]cycloheptene-10-carbonitrile (2a)*

This material was prepared as described by Nauta and co-workers (5) except that dimethyl formamide was used as the reaction medium. The yield was 90%.

The ethylene ketal **2***c* was prepared by heating under

reflux a mixture of **2***a* (3.0 g), ethylene glycol (4.0 ml), benzene (50 ml), and *p*-toluenesulfonic acid (250 mg) for 2 days. The product (2.9 g) had m.p. 118–120° (from ethanol).

Anal. Calcd. for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.31; H, 4.67; N, 5.28.

*10,11-Dihydro-5,10-(epoxymethano)-5H-dibenzo[a,d]-cyclohepten-13-one (3a)*

A mixture of **2***a* (70.0 g) and sodium borohydride (25 g) in ethanol (800 ml) was stirred and heated under reflux for 16 h. The reaction mixture was evaporated and the residue was dissolved in water. The solution was acidified and extracted with chloroform. Evaporation of the extracts and crystallization of the residue gave 56.5 g (80%) of the lactone, m.p. 148–150°; n.m.r. ($CDCl_3$), τ: 6.92 (1H at C-11, q, $J$ = 5, 17 Hz); 6.33 (1H at C-11, q, $J$ = 5, 17 Hz); 5.91 (1H at C-10, t, $J$ = 5 Hz); 4.03 (1H at C-5, s); 2.69 (8-H aromatic, m).

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.49; H, 4.83.

*5-Formamido-5H-dibenzo[a,d]cycloheptene-10-carbonitrile (2b)*

A mixture of **2***a* (3.3 g), formamide (16 ml), and acetic acid (1.6 ml) was heated under reflux for 1 h. The mixture was poured into water and the precipitate was crystallized from ethanol (charcoal) to give 2.7 g of the formamide (73%), m.p. 204–206°; $\gamma_{max}$ (Nujol) 3300, 2215, and 1660 $cm^{-1}$.

Anal. Calcd. for $C_{17}H_{12}NO$: C, 78.44; H, 4.65; N, 10.76. Found: C, 78.29; H, 4.86; N, 10.91.

*10,11-Dihydro-5,10-(iminomethano)-5H-dibenzo[a,d]-cyclohepten-13-imine (4)*

A mixture of **2***b* (15.0 g), sodium borohydride (15.0 g), and ethanol (300 ml) was heated under reflux for 8 h. The mixture was concentrated and then diluted with water. The precipitate was crystallized from ethanol to give 6.5 g of the title product, m.p. 241–243°.

The mother liquors were evaporated and the residue was chromatographed on a neutral alumina column to give 1.07 g of the lactam **5***a*, m.p. 227–229°, and a further 2.5 g of the title product (total yield 67%); n.m.r. ($CDCl_3$), τ: 7.42 (1H at C-11, q, $J$ = 4, 18 Hz); 6.91 (1H at C-11, q, $J$ = 4, 18 Hz); 6.33 (1H at C-10, t, $J$ = 4 Hz); 4.93 (1H at C-5, s); 4.57 (2H at HN—C—NH, unresolved multiplet); 3.18, 2.93 (8H aromatic, m).

Anal. Calcd. for $C_{16}H_{14}N_2$; C, 82.02; H, 6.02; N, 11.96. Found: C, 82.22; H, 5.99; N, 11.73.

*10,11-Dihydro-5,10-(iminomethano)-5H-dibenzo[a,d]-cyclohepten-13-one (5a)*

A mixture of **3***a* (35.0 g) and ammonium hydroxide (500 ml, $d$ 0.88) was heated in an autoclave for 10 h at 175°. The solid product was collected and crystallized from ethanol to give 30.0 g (88%) of the lactam, m.p. 227–229°; n.m.r. (DMSO), τ: 7.00 (1H at C-11, q, $J$ = 4, 16 Hz); 6.42 (1H at q, $J$ = 4, 16 Hz); 6.18 (1H at C-10, t, $J$ = 4 Hz); 4.98 (1H at C-5, d; singlet after $D_2O$ exchange); 2.75 (8H aromatic, m); 1.6 (NH, m).

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.85. Found: C, 81.39; H, 5.40; N, 5.82.

*Reaction of 2c with Sodium Borohydride*

A mixture of **2***c* (5.0 g), sodium borohydride (5.0 g), and ethanol (100 ml) was heated under reflux for 2 h. The mixture was evaporated, diluted with water and extracted with chloroform. Evaporation of the extracts and crystallization of the residue from chloroform–hexane gave 3.5 g of the ketal **6***c*, m.p. 113–115°; n.m.r. ($CDCl_3$), τ: 6.24 (3H at C-10 and -11, m); 5.88 (4H, ketal, m); 2.78 (8H aromatic, m).

Anal. Calcd. for $C_{18}H_{15}NO_2$: N, 5.05. Found: N, 5.12.

Fractional crystallization of the mother liquors from **6***c* gave 0.9 g of the amide **6***a*, m.p. 172–174° (from isopropanol); $\lambda_{max}$ (EtOH) 265 (ε 680), 272 mμ (ε 502).

Anal. Calcd. for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.16; H, 5.92; N, 4.83.

The original aqueous solution was acidified to give 0.2 g of the acid **6***b*, m.p. 182–184° (from isopropanol); $\lambda_{max}$ (EtOH) 264 mμ (ε 640).

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 73.16; H, 5.55.

Treatment of **6***c* with aqueous sodium hydroxide gave more **6***a* and *b*.

Deketalization of **6***c* (1.9 g) with a mixture of ethanol (25 ml) and 3 *N* HCl (25 ml) at room temperature gave the ketonitrile **9***c* (1.3 g), m.p. 108–110° (from isopropanol); $\lambda_{max}$ (EtOH) 271 mμ (ε 16 050) (unchanged on addition of either 0.1 *N* HCl or 0.1 *N* NaOH).

Anal. Calcd. for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; N, 6.01. Found: C, 82.19; H, 4.52; N, 6.10.

Similar treatment of **6***a* gave the ketoamide **9***a*, m.p. 178–180° (from isopropanol); $\lambda_{max}$ (EtOH) 271 mμ (ε 15 880).

Anal. Calcd. for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.57. Found: C, 76.63; H, 5.08; N, 5.43.

*10,11-Dihydro-12-methyl-5,10-(iminomethano)-5H-dibenzo[a,d]cyclohepten-13-one (5b)*

A suspension of **3***a* (10.0 g) in 40% aqueous methylamine was heated in an autoclave for 8 h at 180°. The solids were crystallized from ethanol to give 9.0 g (87%) of the lactam, m.p. 244–246°.

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.9; H, 6.06; N, 5.62. Found: C, 81.56; H, 5.88; N, 5.33.

The same product (4.8 g) was obtained when **5***a* (5.0 g) was methylated with sodium hydride and methyl iodide in anhydrous benzene.

*10,11-Dihydro-12-ethyl-5,10-(iminomethano)-5H-dibenzo[a,d]cyclohepten-13-one (5c)*

A mixture of **3***a* (7.0 g), ethylamine (15.0 g), and water (50 ml) was kept at 175° for 10 h. The mixture was extracted with methylene chloride and the extracts were washed with 2 *N* HCl and evaporated. The residue was recrystallized from methanol to give 5.68 g (68%) of the lactam, m.p. 250–252°.

Anal. Calcd. for $C_{18}H_{17}NO$: C, 82.40; H, 6.46; N, 5.32. Found: C, 82.20; H, 6.51; N, 5.32.

*10,11-Dihydro-5,10-(iminomethano)-5H-dibenzo[a,d]-cycloheptene Hydrochloride (1a)*

Lithium aluminum hydride (5.0 g) was added portionwise to a stirred suspension of **5***a* (15.0 g) in anhydrous tetrahydrofuran (300 ml). The mixture was heated under reflux for 6 h and then cooled and cautiously

treated with water. The mixture was filtered and the filtrate was evaporated to dryness to leave the oily free base. The hydrochloride salt was crystallized from ethanol–ether to m.p. > 270°; n.m.r. ($CDCl_3$) (free base). $\tau$: 7.72 (NH, s); 6.75 ($CH_2$—CH—$CH_2$, m); 5.27 (1H at C-5); 2.87 (8H aromatic, m).

Anal. Calcd. for $C_{16}H_{16}ClN$: C, 74.56; H, 6.22; Cl, 13.76; N, 5.44. Found: C, 74.54; H, 6.16; Cl, 14.29; N, 5.39.

The *N*-acetyl derivative was prepared by heating the free amine with an excess of acetic anhydride for 2 h on the steam bath. It showed m.p. 210–212° (from isopropanol).

Anal. Calcd. for $C_{18}H_{17}NO$: C, 82.14; H, 6.46; N, 5.32. Found: C, 81.87; H, 6.38; N, 5.26.

The *N*-phenylacetyl derivative was prepared from the free amine, phenylacetyl chloride, and anhydrous pyridine. It had m.p. 122–124° (from isopropanol).

Anal. Calcd. for $C_{24}H_{21}NO$: C, 84.92; H, 6.24; N, 4.13. Found: C, 84.65; H, 6.24; N, 4.01.

The *N*-methyl derivative, **1***b*, was prepared from the amine, formaldehyde, and formic acid. The hydrochloride salt had m.p. 244–247° (from isopropanol); n.m.r. ($CDCl_3$) (free base), $\tau$: 7.61 ($NCH_3$, s); 6.82 ($CH_2$—CH—$CH_2$, m); 5.63 (1H at C-5, s); 2.80 (8H aromatic, m).

Anal. Calcd. for $C_{17}H_{18}ClN$: C, 75.10; H, 6.67; Cl, 13.08; N, 5.15. Found: C, 74.94; H, 6.67, Cl, 12.91, N, 5.37.

*10,11-Dihydro-12-ethyl-5,10-(iminomethano)-5H-dibenzo[a,d]cycloheptene (**1***c*)

A mixture of **5***c* (5.5 g), anhydrous tetrahydrofuran (100 ml), and lithium aluminum hydride (3.0 g) was stirred and heated over reflux for 5 h. The mixture was treated with water, filtered, and the filtrate was evaporated. The residue was converted to the hydrochloride salt (4.1 g) which had m.p. 231–234° (from isopropanol).

Anal. Calcd. for $C_{18}H_{19}ClN$: C, 75.90; H, 6.68; Cl, 12.47; N, 4.92. Found: C, 76.20; H, 6.87; Cl, 12.39; H, 4.68.

*10,11-Dihydro-12-phenethyl-5,10-(iminomethano)-5H-dibenzo[a,d]cycloheptene Hydrochloride (**1***d*)

A mixture of the *N*-phenylacetyl derivative of **1***a* (5.0 g), lithium aluminum hydride (3.0 g), and anhydrous tetrahydrofuran (50 ml) was stirred and heated under reflux for 5 h. The basic product was isolated as described above. The hydrochloride (3.0 g) had m.p. 225–228° (from methanol); n.m.r. ($CDCl_3$) (free base), $\tau$: 7.15 (m); 6.75 (m); 5.38 (1H at C-5, s); 2.80 (13H aromatic, m).

Anal. Calcd. for $C_{24}H_{23}N.HCl.0.5H_2O$: C, 77.71; H, 6.79; Cl, 9.56; N, 3.78. Found: C, 77.71; H, 6.76; Cl, 9.29; N, 3.49.

*11-Bromo-10,11-dihydro-5,10-(epoxymethano)-5H-dibenzo[a,d]cyclohepten-13-one (**3***b*)

A suspension of **3***a* and *N*-bromosuccinimide (1.8 g) in carbon tetrachloride (30 ml) containing a trace of benzoyl peroxide was heated under reflux for 2 h. The mixture was filtered and evaporated and the residue was crystallized from ethanol to give the bromolactone (2.0 g), m.p. 167–169°; n.m.r. ($CDCl_3$), $\tau$: 5.53 (1H at C-10, d, $J$ = 5 Hz); 4.95 (1H at C-11, d, $J$ = 5 Hz); 4.94 (1H at C-5, s); 2.52 (8H aromatic, m).

Anal. Calcd. for $C_{16}H_{11}BrO_2$: C, 60.96; H, 3.72; Br, 25.35. Found: C, 61.24; H, 3.71; Br, 25.08.

*5-Hydroxy-N,N-dimethyl-5H-dibenzo[a,d]cycloheptene-10-carboxamide (**2***d*)

A suspension of **3***b* (0.5 g) in ethanol (20 ml) and dimethylamine (0.5 ml) was kept at room temperature for 18 h and then evaporated. The residue was washed with water and crystallized from methanol to give 0.3 g of the amide, m.p. 230–232°; $\lambda_{max}$ (EtOH) 285 mμ (ε 15 800); n.m.r. (DMSO), $\tau$: 7.08, 6.95 (6H at $CON(CH_3)_2$, s); 4.78 (1H at C-5, s); 2.68, 2.18 (8H aromatic, m).

Anal. Calcd. for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.45; H, 6.13; N, 4.91.

*11-Bromo-10,11-dihydro-12-methyl-5,10-iminomethano-5H-dibenzo[a,d]cyclohepten-13-one (**5***d*)

A suspension of **5***b* (15.11 g), *N*-bromosuccinimide (11.4 g), and benzoyl peroxide (50 mg) in carbon tetrachloride (300 ml) was heated under reflux for 1.25 h. The mixture was filtered, the filtrate was evaporated and the residue was crystallized from ethyl acetate to give isomer A of **5***d* (8.0 g), m.p. 205–207°; $\gamma_{max}$ ($CHCl_3$) 1670 $cm^{-1}$; n.m.r. ($CDCl_3$), $\tau$: 2.79 (8H aromatic, m); 4.07 (1H at C-11, d); 5.19 (1H at C-5, s); 5.77 (1H at C-10, d); 7.02 (N—$CH_3$, s).

Anal. Calcd. for $C_{16}H_{14}BrNO$: C, 62.2; H, 4.27; Br, 24.4; N, 4.27. Found: C, 62.41; H, 4.28; Br, 24.66; N, 4.19.

Chromatography of the mother liquors on silica gel, eluting with benzene–chloroform mixture gave a further 0.5 g of isomer A and 7.0 g of almost pure isomer B of **5***d*. This material was repeatedly crystallized from benzene to give the analytical sample of isomer B, m.p. 183–186°; $\gamma_{max}$ ($CHCl_3$) 1670 $cm^{-1}$; n.m.r. ($CDCl_3$), $\tau$: 2.82 (8H aromatic, m); 4.52 (1H at C-11, d); 5.15 (1H at C-5, s); 5.77 (1H at C-10, d), 6.85 (N—$CH_3$, s.)

Anal. Found: C, 62.07; H, 4.21; Br, 24.50; N, 4.23.

*10,11-Dihydro-11-methoxy-12-methyl-5,10-(iminomethano)-5H-dibenzo[a,d]cyclohepten-13-one (**5***f*) (Isomer A)*

A suspension of **5***d* (6.7 g, isomer A) in a solution of sodium (470 mg) in anhydrous methanol was heated under reflux for 18 h. The solution was evaporated and the residue was washed with water and then crystallized from isopropanol to give 4.0 g of **5***f*, m.p. 190–193°; $\gamma_{max}$ ($CHCl_3$) 1660 $cm^{-1}$; n.m.r. ($CDCl_3$), $\tau$: 2.80 (8H aromatic, m); 5.17 (1H at C-5, s, 5.63 (2H at C-10 and -11, 2d, $J$ = 4 Hz); 6.23 (O—$CH_3$, s); 6.92 (N—$CH_3$, s).

*10,11-Dihydro-11-methoxy-12-methyl-5,10-(iminomethano)-5H-dibenzo[a,d]cycloheptene (**1***f*) Hydrochloride (Isomer A)*

Lithium aluminum hydride (1.2 g) was added to a suspension of **5***f* (3.5 g) in anhydrous tetrahydrofuran (60 ml). The mixture was heated under reflux for 5 h and then treated with water. The mixture was filtered and evaporated and the residue was converted to the hydrochloride salt which was crystallized from methanol to give 2.5 g of product, m.p. 245–248°; n.m.r. ($CDCl_3$) (free base), $\tau$: 7.60 ($NCH_3$, s); 6.84 ($NCH_3$, d, $J$ = 3

Hz); 6.5; (1H at C-10, m); 6.35 ($OCH_3$, s); 5.58 (1H at C-5 and 1H at C-11, s); 2.80 (8H aromatic, m).

Anal. Calcd. for $C_{18}H_{20}ClNO$: C, 71.64; H, 6.64; N, 4.64; Cl, 11.78. Found: C, 71.84; H, 6.59; N, 4.90; Cl, 11.63.

*10,11-Dihydro-11-pyrrolidino-12-methyl-5,10-(imino-methano)-5H-dibenzo[a,d]cyclohepten-13-one (**5e**) (Isomer A)*

A mixture of **5d** (4.7 g) (isomer A) and pyrrolidine (20 ml) was heated under reflux for 3 h and then evaporated. The residue was dissolved in chloroform, washed with water, and evaporated. The residue was crystallized from ethanol to give 3.5 g of **5e**, m.p. 190–192°.

Anal. Calcd. for $C_{21}H_{22}N_2O$: C, 79.21; H, 6.96; N, 8.80. Found: C, 78.91; H, 6.96; N, 8.57.

*10,11-Dihydro-11-pyrrolidino-12-methyl-5,10-(imino-methano)-5H-dibenzo[a,d]cycloheptene (**1e**) (Isomer A)*

Lithium aluminum hydride (3.0 g) was added to a solution of **5e** (3.3 g) (isomer A) in anhydrous tetrahydrofuran (30 ml). The mixture was heated under reflux for 3 h and then worked-up in the usual manner to give the product (2.0 g), m.p. 106–107° (from ethanol).

Anal. Calcd. for $C_{21}H_{24}N_2$: N, 9.17. Found: N, 8.93.

*10-Aminomethyl-10,11-dihydro-5H-dibenzo[a,d]cyclo-hepten-5-one (**9b**) Hydrochloride*

A solution of **6c** (3.0 g) in ethanol (20 ml) and liquid ammonia (15 ml) was hydrogenated at 100 atm and 100° in the presence of Raney nickel catalyst (0.5 g) for 7 h. The crude basic product was dissolved in a mixture of ethanol (20 ml) and 3 *N* HCl (20 ml) and kept overnight. The solution was evaporated and the residue was crystallized from ethanol to give 1.3 g of the hydrochloride, m.p. 265–268°; $\lambda_{max}$ (EtOH) 271 mμ (ε 16 050) (unchanged on addition of 0.1 *N* NaOH solution).

Anal. Calcd. for $C_{16}H_{16}ClNO$: C, 70.20; H, 5.88; Cl, 12.90; N, 5.12. Found: C, 69.98; H, 5.85; Cl, 12.94; N, 5.02.

*10,11-Dihydro-11-dimethylaminomethyl-5H-dibenzo[a,d]-cyclohepten-5-one (**9d**) Hydrochloride*

A mixture of **9b** (5.0 g), formic acid (25 ml), and 37% formaldehyde solution was heated on the steam bath for 2 h and then evaporated and basified. The basic material was converted to the hydrochloride salt which was crystallized from isopropanol, m.p. 242–244°; $\lambda_{max}$ 271 mμ (ε 14 900) (unchanged on addition of either 0.1 *N* HCl or 0.1 *N* NaOH).

Anal. Calcd. for $C_{18}H_{20}ClNO$: C, 71.70; H, 6.66; Cl, 11.75; N, 4.64. Found: C, 71.64; H, 6.80; Cl, 11.69; N, 4.77.

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