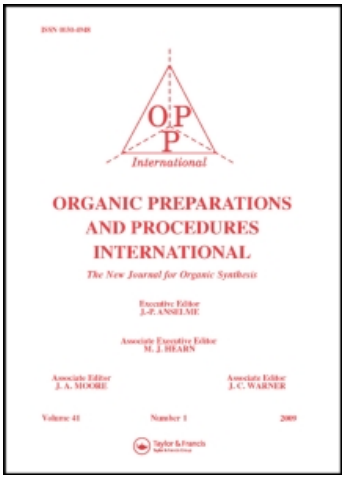

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AN IMPROVED MEDIUM-SCALE PREPARATION OF DIBENZO[*a, e*] CYCLOOCTEN-5(6*h*), 11(12*h*)DIONE

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AN IMPROVED MEDIUM-SCALE PREPARATION OF DIBENZO[*a*,*e*] CYCLOOCTEN-5(6*H*), 11(12*H*)DIONE

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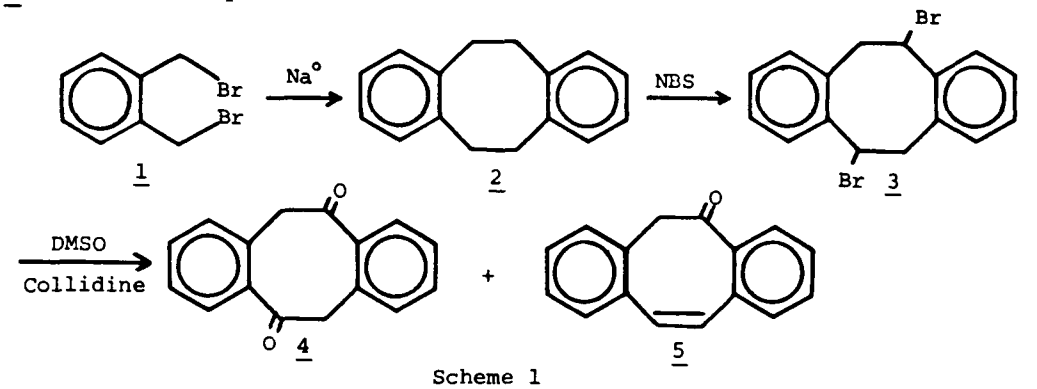
In connection with a project which produced polymers of novel structure,[1] we required a route to ten-gram quantities of dibenzocyclooctanedione, 4, which was first prepared in a pioneering effort by Wawzonek,[2] and subsequently by Yates.[3] We describe here some of our results in developing a process which entails a 9-step synthesis from commercially-available 7 to 4 in an overall yield of 15%.

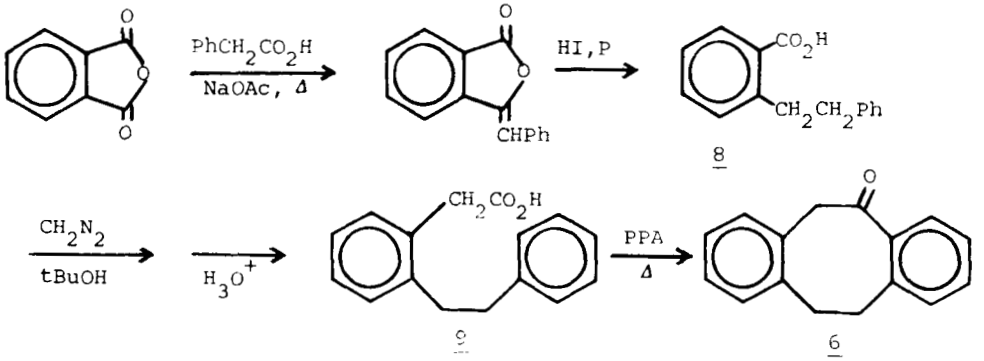


Scheme 1

Yates, Lewars and McCabe[3] prepared 4 by coupling dibromide 1 to 5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene (2) followed by bromination to 5,11-dibromo-5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene, (3) and then oxidation with dimethyl sulfoxide and collidine to give a mixture of 4 and dibenzo[*a*,*e*]cycloocten-5(6*H*)-one (5) [Scheme 1]. The overall yield from xylene to purified product was about 5%. Although the coupling of α,α'-dibromo-*o*-xylene with sodium in dioxane is reported to give 2 in 33-40%

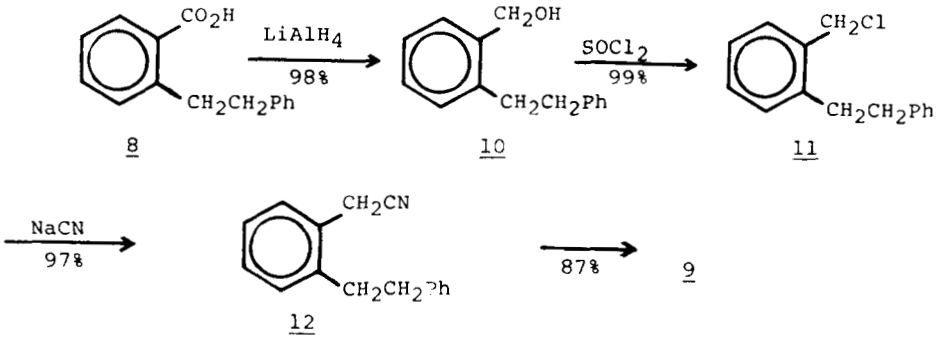
yield, in our hands, even at very high dilution, the best yields obtained were 12-17%. Yates and coworkers had shown that by-product 5 could be catalytically reduced to the corresponding saturated ketone 6 in essentially quantitative yield and that this ketone could be converted to 2 by a Wolff-Kishner reduction (no yield given). Thus, if a process for the preparation and conversion of saturated ketone 6 to hydrocarbon 2 could be developed, a more efficient route to 4, which included recovery of starting materials and recycling of a by-product, would be available.

Ketone 6 was originally prepared by Cope and Smith[4] from phthalic anhydride as shown in Scheme 2 in 30-34% overall yield; these authors report a 75% yield for the Wolff-Kishner reduction of 6 to 2.



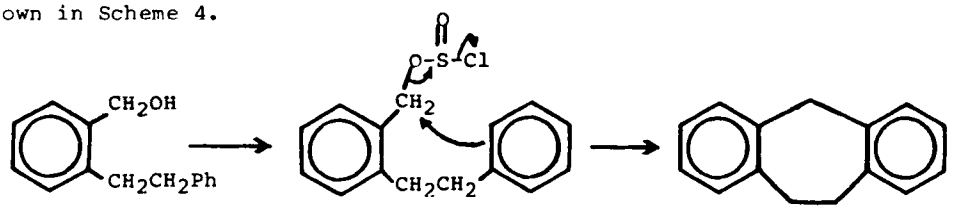
Scheme 2

On the scale which we envisioned, the use of the requisite amounts of diazomethane posed a serious problem. An alternative route from acid 8 to homolog 9 was developed as shown in Scheme 3; compounds 11 and 12 could be



Scheme 3

used without purification. Attempted conversion of nitrile 12 directly to ketone 6 using polyphosphoric acid resulted only in the formation of *o*-phenethylacetamide (13). When the homologous acid 9 was purified by dissolution in sodium bicarbonate solution a small amount of 10,11-dihydro-5*H*-dibenzo[*a*,*e*]cycloheptene (14) which failed to dissolve could be isolated. Hydrocarbon 14 presumably arose from intramolecular reaction of some cationic species, perhaps derived from the intermediate chlorosulfite, as shown in Scheme 4.

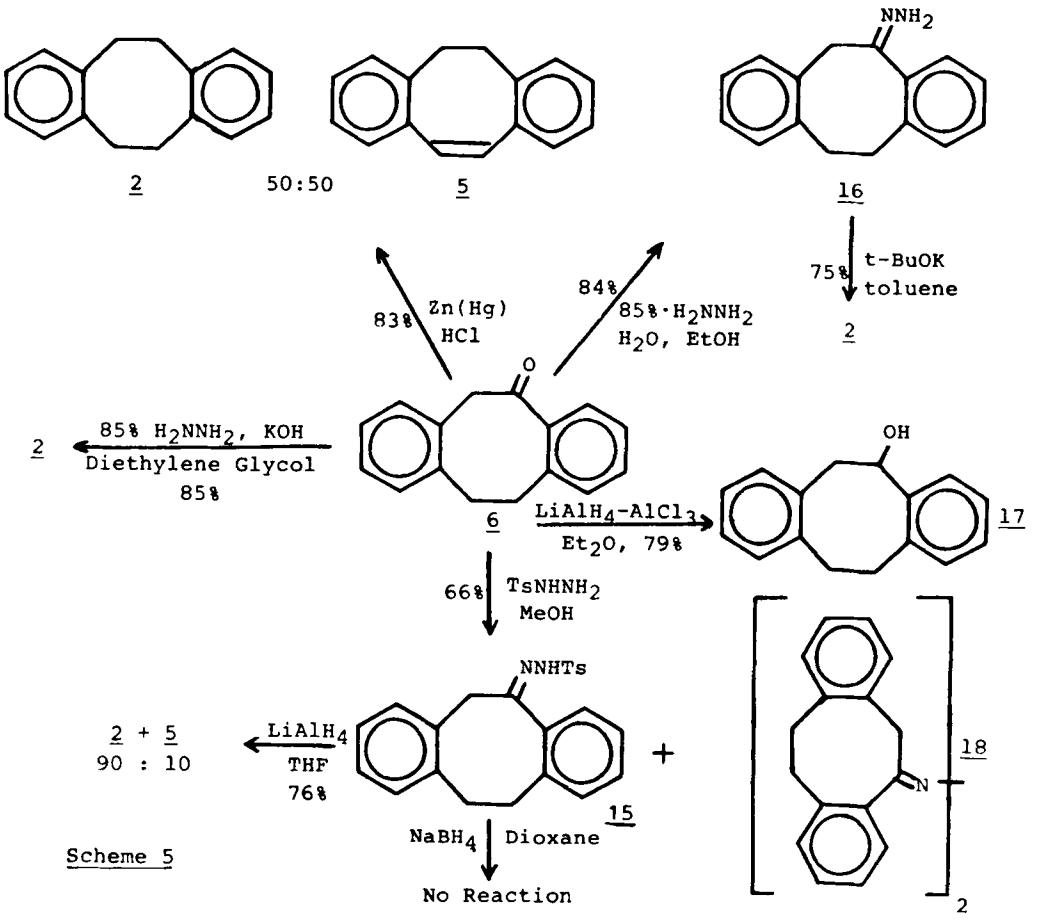


10 14

Scheme 4

Several methods have been reported to give high yields in the conversion of ketones to hydrocarbons: the reduction of tosylhydrazones with lithium aluminum hydride in THF[5] or sodium borohydride in dioxane,[6] the Wolff-Kishner reduction[7] in DMSO at room temperature,[8] in refluxing toluene[9] or diethylene glycol;[3,4] reduction using $LiAlH_4$-$AlCl_3$[10]; or the Clemmensen reduction.[11] Scheme 5 illustrates a summary of the results found in this survey. The most reliable results were obtained from the Wolff-Kishner reduction using 85% hydrazine hydrate followed by potassium t-butoxide in refluxing toluene[9] or potassium hydroxide in diethylene glycol.[3,4] These methods gave 2 as the sole product in yields of 75-85%.

Hydrocarbon 2 was converted to dibromide 3 using N-bromosuccinimide[12] according to the method of Cope and Fenton[13] which was reported to give from 70 to 88% yield. Later work by Yates *et al.*[3] reported consistent yields of about 75%. It was found in this work that by a slight modification of the isolation procedure, consistent yields above 95% could be obtained (see Experimental). Finally, reaction of 3 according to the method



Scheme 5

of Yates *et al.*[3] gave, as reported, a mixture of unreacted dibromide 3, enone 5, and the desired diketone 4. Separation by column chromatography on silica gel gave the purified product in an overall 15% yield.

EXPERIMENTAL SECTION

All melting points are uncorrected and were determined in capillary tubes with a Thomas-Hoover Unimelt apparatus. Nuclear magnetic resonance (NMR) spectra were obtained on Varian T-60 and CFT-20 spectrometers and are reported in δ units using tetramethylsilane as an internal standard. Infrared spectra (IR) were recorded on a Perkin-Elmer model 521 spectrophotometer with the following band intensity notations being used: vs = very strong, s = strong, m = medium and w = weak; for known compounds only characteristic bands are given. Ultraviolet spectra (UV) were recorded on a Cary 14 spectrophotometer. Mass spectra were taken on a CEC 21-104 mass spectrometer operating at 70 eV and are reported as m/e with relative intensity (percent of base peak) in parentheses. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Gas chromatography-mass spectral data (GC-MS) was obtained on a Varian MAT 111 instrument using an electron impact detector. A 10 foot glass column (2 mm I.D.) packed with OV-17 on 100-120 mesh Gas Chrom Q was used. The instrument was programmed

from 30° to 300° at 20°/min using Helium as the carrier gas. Thin layer chromatography (TLC) analyses were obtained using 50 mm x 100 mm silica gel coated glass slides which were purchased from VWR Scientific, Rochester, NY. The developed TLC plates were visualized with a USVL25 Mineralight® emitting short or long wavelength ultraviolet light (Ultraviolet Products, San Gabriel, California). Extractions were usually completed by washing finally with a saturated sodium chloride solution, drying over anhydrous magnesium sulfate followed by vacuum filtration and evaporation of solvent under vacuum on a rotary evaporator at room temperature up to 100°.

o-(α-Phenethyl)benzoic Acid (8).- The method of Cope and Fenton[13] was used starting with 222 g of benzalphthalide (Aldrich). The solid obtained by this procedure was recrystallized (70% EtOH/H_2O, v/v) giving 166 g (73%) of 8, mp. 132-133°, lit.[13] mp. 129-130°.

IR (KBr): 1690s (C=O), 913s (OH, def.) and 755s cm^{-1} (aryl H); ^1H NMR (DMSO-d_6): 3.06 (m, 4H, CH_2CH_2), 7.10-7.50 (m, 9H, aryl CH) and 12.78 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): 169.17 (C=O), 126-143(12 peaks, aromatic) 36.42 and 37.82 ppm (CH_2CH_2); mass spectrum m/e (rel. intensity): 226 (M^+, 25).

o-Phenethylbenzyl Alcohol (10).- To a 5 L three-necked flask was added 31.1 (0.82 mol) of lithium aluminum hydride and 1.9 L of dry diethyl ether. While vigorously stirring the ethyl ether-lithium aluminum hydride mixture, a solution of 147.5 g (0.65 mol) of o-phenethylbenzoic acid (8) in 750 mL of dry tetrahydrofuran (distilled from sodium hydride) was added dropwise. At the end of the addition, excess $LiAlH_4$ was destroyed by slow addition of 25 mL of water followed by the addition of one liter of 10% H_2SO_4. The layers were separated and the ether layer was washed successively with 10% $NaHCO_3$, saturated NaCl solution, and distilled water. The ether layer was dried ($MgSO_4$) and concentrated in vacuo. The residue crystallized on standing. Recrystallization (hexane) gave 135 g (98%) of 10, mp. 56-58°, lit.[14] 58°.

IR (KBr); 3325-3220s (OH), 1004s (OH def), and 755 s cm^{-1} (4 adjacent ring H); ^1H NMR ($CDCl_3$): δ 1.60 (broad s, 1H, OH), 2.93 (s, 4H, CH_2CH_2), 4.60 (s, 2H, CH_2-O) and 6.96-6.47 (m, 9H, ArH); ^{13}C NMR ($CDCl_3$): 122-141 (12

peaks, aromatic), 62.62 ($ArCH_2OH$) 37.59 and 34.28 ppm (ϕ CH_2CH_2Ar); mass spectrum m/e (relative intensity): 194 (loss of H_2O, 89), 179 (loss of $H+CH_3OH$, 40) and 91 (C_7H_7, 100).

o-Phenethylbenzyl Chloride (11).- To one liter of benzene dried by azeotropic distillation, was added 107.3 g (0.83 mol) of thionyl chloride from a freshly opened bottle. To this solution in a 3 L flask was added one drop of pyridine followed by a solution of 135.4 g (0.64 mol) of *o*-phenethylbenzyl alcohol in 500 mL of benzene. At the end of the addition, the reaction mixture was refluxed on a water bath for 2 hr. Benzene was removed by vacuum distillation. The residue was redissolved in diethyl ether and washed sequentially with 10% $NaHCO_3$, a saturated NaCl solution and distilled water. Drying ($MgSO_4$) and concentration gave 145.8 (99%) of halocarbon 11. The compound was used without further purification. ^1H NMR ($CDCl_3$): δ 2.96 (s, 4H, CH_2CH_2), 4.48 (s, 2H, $-CH_2Cl$) and 7.0-7.66 (m, 9H, ArH).

o-Phenethylbenzyl Cyanide (12). - To a 500 mL flask was added 32.4 g (0.66 mol) of sodium cyanide followed by 36 g of water. This mixture was heated on a water bath at 85° until the sodium cyanide dissolved. To this solution was added a mixture of 117 g (0.508 mol) of *o*-phenethylbenzyl chloride (11) and 120 g of ethanol (compound 11 was insoluble in ethanol at room temperature). This mixture was heated at 85° on a water bath for 4 hr and then cooled to room temperature and filtered. The solid was washed with ethanol. The filtrate was transferred to a separatory funnel, the bottom layer was separated and the upper, aqueous layer was extracted once with an equal volume of diethyl ether. The bottom layer was returned to the funnel with the ether solution, diluted with water and ether and washed with water until the bottom aqueous layer was neutral to litmus paper. The ethereal solution was dried ($MgSO_4$) and concentrated to yield 109 g (97%) of product, identified by ^1H NMR and used without further purification.

^{1}H NMR ($CDCl_3$): δ 2.83 (s, 4H, $ArCH_2CH_2Ar$), 3.37 (s, 2H, $ArCH_2CN$) and 6.67-7.40 (m, 9H, Ar-H).

o-Phenethylphenylacetamide (13) from the attempted Synthesis of 11,12-Dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one (6) from (12).- A mixture of 1.0 g (4.5 mmol) of *o*-phenethylbenzyl cyanide (12) and 50 g of polyphosphoric acid was heated at 90° and stirred for 4 hr. Then 8 mL of water was added to the reaction mixture causing the internal temperature to increase to 120°. This mixture was stirred for an additional hour, was cooled and poured into 300 mL of water. The precipitated solid was collected by filtration, washed successively with water, 10% Na_2CO_3 solution and water. The solid was dried and recrystallized from benzene-hexane to give 0.93 g (86.5%) of white needles. The solid was identified as *o*-phenethylphenyl acetamide (13), mp. 124-126°.

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.4; H, 7.12; N, 5.86; O, 6.69.

Found: C, 80.7: H, 7.3; N, 5.7.

IR (KBr): 3390s (amide NH) and 1660s cm^{-1} (amide C=O); ^{1}H NMR ($CDCl_3$): δ 2.98 (s, 4H, $ArCH_2CH_2Ar$), 3.61 (s, 2H, $ArCH_2C=O$), 5.0-6.3 (very broad, NH), 7.26-7.57 (m, 9H, ArH); ^{13}C NMR ($CDCl_3$) 174.07 (C=O), 141.35, 140.52, 133.14, 130.69, 129.88, 128.43, 127.83, 126.75, 126.07, 40.68 ($ArCH_2C=O$), 3715 and 34.81 ppm (Ph CH_2CH_2-Ar); mass spectrum m/e (rel. intensity): 239 (M^+, 82), 148 (78), 131 (100), 105 (35), 104 (41), 103 (79), 91 (73) and 77 (22).

o-(Phenethyl)phenylacetic Acid (9).- To 109 g (0.49 mol) of *o*-(2-phenethyl) benzyl cyanide (12) in a one liter flask was added 200 mL each of distilled water, concentrated H_2SO_4, and finally glacial acetic acid. This mixture was stirred and refluxed for 2 hr. The reaction mixture was cooled and poured with vigorous stirring into 2 L of water. The precipitate was collected by filtration, washed with dilute H_2SO_4 solution and air-dried. It was then dissolved in a Na_2CO_3 solution (212 g of Na_2CO_3 in

1 L of water), stirred for 2 hr and allowed to stand overnight. A white, crystalline solid which collected at the bottom of the flask was collected by vacuum filtration and washed with water until neutral. The solid was identified as 10,11-dihydro-5 -dibenzo[*a*,*e*]cycloheptene (14), mp. 74-76° lit.[14] 75°.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.7; H, 7.3.

Found: C, 92.5; H, 7.6.

^{1}H NMR ($CDCl_3$): δ 3.21 (s, 4H, $ArCH_2CH_2Ar$), 4.19 (s, 2H, $ArCH_2Ar$), and 7.23 (s, 8H, ArH); ^{13}C NMR ($CDCl_3$): 139.18, 138.90, 129.48, 128.91, 126.52, 125.98, 40.91 ($ArCH_2Ar$) and 32.44 ppm ($ArCH_2CH_2Ar$); mass spectrum m/e (rel. intensity) 194 (M^+, 100).

The filtrate obtained after isolation of 14 was acidified with 25% aqueous H_2SO_4. The acidic solution was added slowly to the filtrate cooled in an ice bath. The white precipitate was collected by vacuum filtration, washed with 5% H_2SO_4 and air-dried overnight. The yield of 9 was 103.4 g, (87.4%, mp. 86-88°, lit.[4] 92.2-93.2°.

^{1}H NMR (benzene-d_6): δ 2.76 (s, 4H, $ArCH_2CH_2\phi$), 3.31 (s, 2H, $ArCH_2COOH$), 7.0-7.3 (m, 9H, ArH) and 11.26 (s, 1H, COOH).

11,12-Dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one (6).- To a 3 L flask was added 86.8 g (0.36 mol) of o-(2-phenethyl)phenylacetic acid (9) and 2795 g of polyphosphoric acid. This mixture was stirred and heated on a boiling water bath for 3 hr and then cooled to room temperature and poured with vigorous stirring into 6 L of water. The solid which separated was collected by filtration and dissolved in 200 mL of methanol. This concentrated solution was poured rapidly into 3.5 L of water. The milky solution was allowed to stand for one hour and the resulting white needles were vacuum filtered and washed with water. The solid was dried overnight in a vacuum oven (50°/25 torr) and stored in a desiccator over P_2O_5. The yield of 6 was 74.7 g (93.5%), mp. 93-95°, lit.[3] 92-95°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.4; H, 6.3; O, 7.2.

Found: C, 86.0; H, 6.3.

IR (KBr): 1675s cm^{-1} (ketonic C=O); ^1H NMR ($CDCl_3$): δ 3.33 (s, 4H, $ArCH_2CH_2Ar$); 4.22 (s, 2H, $ArCH_2C=O$) and 7.06-7.70 (m, 8H, Ar-H) ^{13}C NMR ($CDCl_3$) 204.0 (C=O), 138.35, 137.86, 133.56, 131.44, 130.81, 130.46, 129.61, 128.35, 128.01, 127.31, 126.58, 126.49, 51.40 ($ArCH_2C=O$), 34.70 and 33.62 ppm ($ArCH_2CH_2Ar$); mass spectrum m/e (rel. intensity): 222 (M^+, 100).

11,12-Dihydro-5(6*H*)-hydroxydibenzo[*a*,*e*]cyclooctene (17) from the Attempted Synthesis of 5,6,11,12-Tetrahydrodibenzo[*a*,*e*]cyclooctene (2) by $LiAlH_4$-$AlCl_3$[10] Reduction of (6).- A solution of 0.38 g (10 mmol) of $LiAlH_4$ in 10 mL of diethylether was placed in a 100 mL flask. A solution of 1.35 g (10 mmol) of granular $AlCl_3$ in 10 mL of diethyl ether was added rapidly. After five minutes a solution of 1.8 g (8 mmol) of 11,12-dihydrodibenzo-[*a*,*e*]-cycloocten-5(6*H*)-one 6 and 1.0 g (7.5 mmol) of $AlCl_3$ in 20 mL of diethyl ether was added so that a gentle reflux was maintained. After addition, the reaction mixture was stirred for 30 min. Water (10 mL) was added slowly followed by 15 mL of 6N H_2SO_4. The layers were separated and the aqueous layer was washed with an equal volume of ether. The ether layers were combined, washed successively with 10% $NaHCO_3$, and water and then dried ($MgSO_4$). Concentration gave 1.42 g (79%) of a compound identified as 11,12-dihydro-5(6*H*)-hydroxydibenzo[*a*,*e*]cyclooctene 17, mp. 113-116°, lit.[3] 114.2-115.5°.

^1H NMR ($CDCl_3$): δ 2.10 (s, 1H, OH), 2.8-3.7 (m, 6H, CH_2), 5.13 (t, 1H, J=8 Hz, $-CH_2-CH(OH)Ar$), and 6.7-7.2 (m, 8H, Ar-H); ^{13}C NMR ($CDCl_3$): 141.56 (C-4b), 139.21 (C-4a), 137.94 (C-6a), 137.53 (C-10a), 130.02 (C-2, C-3), 129.85 (C-8, C-9), 127.45 (C-4), 126.95 (C-1), 126.38 (C-7), 126.00 (C-10), 74.62 (C-5), 43.76 (C-6), 35.03 (C-12), and 33.61 ppm (C-11).

Attempted Synthesis of 5,6,11,12-Tetrahydrodibenzo[*a*,*e*]cycloocten (2) by Clemmensen Reduction[11] of 6.- To a one liter flask was added 200 g of

mossy zinc which was covered with 500 mL of 15% NaOH solution. The mixture was heated to 60° and stirred for 2 hr. The caustic solution was decanted and the zinc was washed with distilled water until neutral to litmus. It was then covered with a solution of 15 g of $HgCl_2$ and 10 mL of concentrated HCl in 250 mL of water. The mixture was stirred for one hour, the solution was decanted and the zinc amalgam was washed with distilled water. The solid was covered with 150 mL of water, 200 mL of concentrated HCl and a hot solution of 20 g (0.09 mol) of 6 in 200 mL of 95% ethanol. The mixture was refluxed for 5 hr while HCl gas was bubbled through the reaction mixture. The hot solution was poured into an ice-water mixture and the pale yellow solid was collected by filtration and was dissolved in diethyl ether. The ether solution was washed successively with 10% $NaHCO_3$ solution, water, a saturated NaCl solution and finally water. The ether solution was dried ($MgSO_4$) and concentrated to give 15.63 g (83.5%) of a pale yellow solid. The solid was dissolved in boiling hexane, shaken one hour with silica gel (10 g), filtered and concentrated to give a white solid, mp. 66-80°.

Analysis by thin layer chromatography on silica gel showed one spot when developed with 5% diethylether-95% hexane with an R_f value identical with 2 (R_f = 0.68). GC-MS analysis showed the product to be a mixture of equal amounts of 2 and 5.

Mass spectrum m/e (rel. intensity): for 2, 208 (M^+, 90), 193 (100), 178 (42), 115 (44) and 104 (72), and for 5, 206 (M^+, 90), 205 (100), 191 (25), 101 (37), 100 (61), 88 (77), 76 (48) and 17 (43).

11,12-Dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one Tosyl hydrazone (15).- 11,12-Dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one(6), 5 g (23 mmol) and 6.03 g (0.32 mol) of p-toluenesulfonylhydrazine were added to a flask containing 200 mL of methanol. This solution was refluxed for 4 hr. A yellow solid precipitated and was collected by filtration after cooling to room

temperature. The filtrate was concentrated causing crystallization of a white solid. The solid was collected by vacuum filtration and recrystallized from methanol to give long needles, mp. 188-190°.

Anal. Calcd for $C_{23}H_{22}N_2SO_2$: C, 70.77; H, 5.64; N, 7.18; S, 8.20; O, 8.20.

Found: C, 7.6; H, 5.9; N, 7.4; S, 8.4.

IR (KBr): 3280w, 3210m, 1595m, 1165vs, 768s, 673s and 541s cm^{-1}; ^1H NMR (acetone-d_6): δ 2.51, 2.56 (2s, 3H, Ph-CH_3), 2.93, 2.98 (2s, 1H, NH): 3.11 (s, 4H, $ArCH_2CH_2$), 4.10, 4.20 (2s, 2H, CH_2 C=N-), 7.03-7.40 (Ar-H), 7.25 (d, 2H, J=8 Hz, H ortho to CH_3) and 8.05 (d, 2H, J=8 Hz, H ortho to O=S=O); ^{13}C NMR (acetone-d_6): 143.89, 138.54, 131.08, 130.42, 130.26, 129.64, 129.54, 129.34, 128.84, 128.14, 128.06, 127.27, 126.78, 126.51, 126.13, 35.68 ($ArCH_2C$=N), 33.28 and 32.81 ($ArCH_2CH_2Ar$) and 20.82 ppm ($ArCH_3$); mass spectrum m/e (rel. intensity): 391.8 (M^+, 0.70), 235 ($C_{16}H_{15}N_2$, 100).

The yellow compound isolated at the end of the reaction was shown to be the azine 18, mp. 243-246°.

IR (KBr): 301 w, 2900w, 1685w, 1597m, 1490m, 1023m, 773s, 758s, 745s, 638m and 628m cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.15 (s, 4H, $ArCH_2CH_2Ar$), 4.03 (s, 2H, Ar-CH_2-C=N)), and 7.1-7.6 (m, 8H, Ar-H); mass spectrum m/e (rel. intensity) 400 (M^+, 100), 335 (15), 135 (14), 222 (18), 221 (23), 220 ($M^+-C_{16}H_{14}N$, 56), 219 (29), 218 (73), 217 (14), 206 (12), 205 (46), 204 (36), 203 (13), 193 (18), 179 (10), 178 (16), 116 (12), 114 (14), 105 (10), 104 (12), 103 (12), 91 (18) and 18 (16).

Reduction of Tosylhydrazone 15 with $LiAlH_4$.- To a 100 mL reaction vessel equipped with a mechanical stirrer and a condenser was added 1.4 g (37 mmol) of $LiAlH_4$, 50 mL of dry tetrahydrofuran and 1.0 g (2.6 mmol) of tosylhydrazone 15. The mixture was stirred and refluxed for 48 hr. Samples were withdrawn from the reaction mixture at 1 hr, 4 hr and 24 hr. Analysis by TLC (5% diethyl ether-95% hexane) showed unreacted hydrazone

(R_f = 0) after 24 hr. Continuing the reaction for 48 hr resulted in complete disappearance of the hydrazone 15 when analyzed by TLC. Ethanol was added slowly to destroy excess $LiAlH_4$ followed by diethyl ether, water, and finally concentrated H_2SO_4 until the mixture was acidic. The aqueous layer was separated while the ether layer was washed with water until neutral, dried ($MgSO_4$) and concentrated. The residue, a clear colorless liquid was shown by TLC on silica gel to be different (R_f = 0.45) from the expected product 5,6,11,12-tetrahydro-dibenzo[*a*,*e*]cyclooctene (2) (R_f = 0.37 when developed with 5% diethyl ether-95% hexane). The product was shown by GC-MS analysis to be mostly 5,6-dihydrodibenzo[*a*,*e*]cyclooctene (5) contaminated with approximately 10% of 2.

Mass spectrum m/e (rel. intensity): for the peak representing 10% of the mixture, 208 (M^+, 55), 193 (loss of CH_3, 100); and for the peak representing 90% of the mixture, 206 (M^+, 100), 191 (loss of CH_3, 73).

Wolf-Kishner Reduction of 11,12-Dihydrodibenzo[*a*,*e*]cycloocten-5(6*H*)-one (6) with Potassium t-Butoxide[9].- To a one liter flask fitted with an efficient condenser was added 25 g (0.112 mol) of 6, 60 g of 85% hydrazine hydrate and 550 mL of ethanol. This solution was refluxed for 24 hr under N_2. The ethanol was removed under vacuum and the residue was dissolved in diethyl ether, washed once with a saturated NaCl solution and dried ($MgSO_4$). Concentrating the solution gave 22.4 g (84%) of a solid residue shown to be 16 by ^1H NMR: 3.15 (s, 4H, $ArCH_2CH_2Ar$), 3.88 (s, 2H, $ArCH_2C{=}N$), 5.47 (broad s, 1H, NH_2) and 7.0-7.5 (m, 8H, ArH). The crude solid was not purified further but was dissolved in 200 mL of dry toluene. This solution was added to a mixture of 12.5 g (0.11 mol) of potassium t-butoxide in 600 mL of dry toluene. The mixture was stirred and refluxed for 24 hr, then cooled and poured into a solution of 100 mL of concentrated HCl in 2 L of water. The toluene layer was separated and washed with water until neutral. The solution was dried ($MgSO_4$) and concentrated to give 14.2 g of

product which was dissolved in boiling hexane, treated with silica gel (10 g), filtered and concentrated to give a solid which afforded 13.91 g (75%) of 2 when crystallized from 95% EtOH, mp. 109-110° lit.[13] 108.5-109°. IR (KBr): 1485s, 1445s, 1042m, 925m, 762vs, 750vs, and 540vs cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.05 (s, 8H, $ArCH_2CH_2Ar$) and 6.96 (s, 8H, Ar-H); ^{13}C NMR ($CDCl_3$): 140.60 (C-4a, C-6a, C-10a, C-12a), 129.63 (C-2, C-3, C-8, C-9), 126.08 (C-1, C-4, C-7, C-10), and 35.15 ppm ($ArCH_2CH_2Ar$); mass spectrum m/e (rel. intensity) 208 (M^+, 60), 193 (100), 179 (46), 178 (50), 117 (22), 116 (39), 115 (38), 104 (42), 103 (26), 91 (22), and 78 (25).

Wolff-Kishner Reduction of 6 (KOH in Diethylene Glycol)[3,4].- In a 250 mL flask was placed 10 g (0.18 mol) of KOH, 15 mL of 85% hydrazine hydrate and 100 mL of diethylene glycol. To this stirred mixture 5.0 g (22.6 mmol) of 6 was added. The mixture was heated at 137° for 2 hr after which excess water and $NH_2NH_2 \cdot H_2O$ were distilled until the temperature reached 200°. The solution was refluxed at 190-200° for 3 hr, cooled and poured into 800 mL of water acidified with 30 mL of concentrated HCl. The solid which formed was filtered, dissolved in diethyl ether and the ether solution was washed with water until neutral. The solution was dried ($MgSO_4$) and concentrated to give a solid which was redissolved in hexane and filtered through silica gel. Recovery of the solid and recrystallization from ethanol gave 3.8 g (66%) of a white, crystalline solid, mp. 108.5-109°, lit.[13] 108.5-109°.

The ^1H NMR spectrum was identical with an authentic sample of 2.

5,11-Dibromo-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (3).- The procedure of Cope and Fenton[13] was used. 5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene (2), 27.5 g (0.13 mol), and 46 g (0.26 mole) of N-bromosuccinimide were added to 350 mL of CCl_4. This mixture was stirred and refluxed for one hour. The reaction mixture was then cooled and filtered. The filtrate was concentrated to give 28.2 g (59%) of 3. The solid residue,

which was mostly succinimide, was boiled in CCl_4 and filtered while hot to recover additional product. The filtrate was concentrated to give more solid which was washed extensively with water and air-dried. The total amount of solid 3 isolated was 47.3 g (98%), mp. 179-183°. The solid obtained was used without further purification. However, a small sample recrystallized from 95% EtOH raised the melting point to 181-183°, lit.[13] 188-189°, lit.[3] 185-186°.

^1H NMR ($CDCl_3$): δ 3.82 (2d, 2H, J_{AB} = 15 Hz, J_{AX} = 9 Hz, CHCHBr) 4.55 (2d, 2H, J_{BA} = 15 Hz, J_{BX} = 11 Hz, CHCHBr), 5.63 (2d, 2H, J_{AX} = 9 Hz, J_{BX} = 11 Hz, CH_2CHBr) and 7.27-7.53 (m, 8H, Ar-H).

Dibenzo[*a,e*]cycloocten-5(6*H*),11(12*H*)-dione (4).- The procedure of Yates, Lewars and McCabe[3] was used. A mixture of 37.3 g (0.102 mol) of 5,11-dibromo-5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctene 3 and 41.6 g (0.344 mol) of collidine in 560 mL of DMSO was heated and stirred at 130° for 1.3 hr. The reaction mixture was then cooled and poured into 2.8 L of ice water. The solid which separated was filtered and collected. The air-dried solid weighed 20.77 g and was analyzed by TLC on silica gel. Development with methylene chloride revealed three spots; the starting compound 5 (R_f = 0.80), dibenzo[*a,e*]cyclooctene-5(6*H*)-one (5) (R_f = 0.60), and dibenzo[*a,e*]cyclo-octene-5(6*H*),11(12*H*)-dione (4) (R_f = 0.33). Washing the solid with two 500 mL portions of hexane removed all impurities except the enone 5 and the dione 4 (yield 17 g). GC-MS analysis showed the dione to be present in greater amount (85% vs 15%). Mass spectrum of 5, m/e (rel. intensity): 220 (M^+, 100), 219 (73), 192 (32), 191 (74), 189 (39), 94 (66), 82 (49), 81 (28), 17 (74); mass spectrum of 4: 236 (M^+, 100), 208 (76), 207 (64), 202 (37), 179 (60), 178 (42), 94 (35), 89 (97), 88 (89), 76 (36), 63 (28). The enone-dione mixture was separated on a column (5.5 x 200 cm) of silica gel by eluting with CH_2Cl_2 to isolate the enone (3.7 g) followed by CH_2Cl_2 containing 1% EtOH to obtain the dione (8.8 g, 36%

yield): mp. 202.5-204.5°, lit.[2] mp. 203.5-204.5°.

^{1}H NMR ($CDCl_3$): δ 4.57 (s, 4H, CH_2C), 7.27-7.73 (m, 6H, ArH, 7.87-8.13 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$): 198.45 (C=O), 136.12, 132.89, 132.68, 131.11, 130.06, 128.18 (6 peaks, aromatic carbon atoms) and 51.91 ppm (CH_2C=O).

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