Meerwein Arylation of Methyleneglutaronitrile with Anthraquinone Diazonium Hydrogensulfate. Synthesis of an Enolizable Benzanthrone Lactone

P. Sutter and C. D. Weis*

Dyestuffs and Chemicals Department, CIBA-GEIGY Ltd.,
Basel, Switzerland

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The Meerwein reaction of 1-anthraquinone diazonium hydrogensulfate with 2-methyleneglutaronitrile in methanol yielded predominantly 3-hydroxy-4-(1-anthraquinone)-1,3-butanedicarbonitrile (**5**), while the corresponding 2-methyleneglutaric acid diethyl ester furnished a derivative of 1-(anthraquinone)butanolide **10**. Catalytic dehydrocyanation of **5** was effected with Dowex-50 to furnish 3-oxo-4-(anthraquinone)butanecarbonitrile (**6**). Both nitriles **5,6** gave in a double cyclization reaction a benzanthrone lactone **12** from which a crystalline derivative of the enol form was isolated, the structure of which was elucidated by ^{1}H- and ^{13}C-nmr spectra. The methylene group of the lactone ring underwent coupling reactions with aromatic diazonium salts to form hydrazone derivatives.

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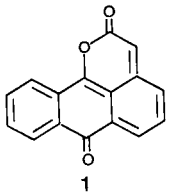
Introduction.

The Meerwein reaction of unsaturated compounds with 1-anthraquinone diazoniumhydrogensulfate yielded anthraquinone derivatives which are substituted at C-1 [1, 2a,b]. Analogously, the 1,5-anthraquinone bis-diazonium salts have thus provided an easy access to C-1 and C-5 disubstituted anthraquinones, which subsequently underwent a double ring closure to provide anthradipyrans [3]. The C-1 substituted derivatives have led to a convenient synthesis of 2-hydroxybenzanthrone [2b], and further to heterocyclic polynuclear structures such as 2*H*,7*H*-dibenzo[*de*,*h*]chromene-2,7-dione (pyranthrone) (**1**) [4a,b], or to 1-aza-2-hydroxybenzanthrone (**2**) [5a,b,6].



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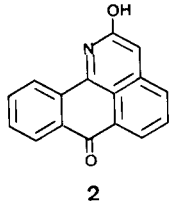


2

The common precursor of **1** and **2** is the 1-(anthraquinone)acetic acid which was prepared by Meerwein arylation of 1,1-dichloroethylene with anthraquinone diazoniumhydrogensulfate, followed by acid hydrolysis of the dichloromethylene group [1]. This reaction adds a fragment, consisting of two carbon atoms, to the anthraquinone system. Similarly, the linkage of a three-carbon unit with anthraquinone is demonstrated by the reaction of methacrylonitrile with the anthraquinone diazonium salt, furnishing 1-(2-oxopropyl)anthraquinone which, without having been isolated, was cyclized to 2-hydroxybenzanthrone [2a,b].

The attachment of a linear structured olefinic fragment consisting of five carbon atoms to the anthraquinone system has not yet been reported. This paper deals with the addition of 2-methyleneglutaronitrile (**4**) to the carbon atom C-1 of anthraquinone by a Meerwein reaction and the facile subsequent ring closure of the product obtained, to furnish a substituted benzanthrone derivative. This method provided a convenient access to the hitherto unaccesible lactone of 2-hydroxybenzanthrone-1-acetic acid (1*H*-anthra[1,9-*ef*]benzo[*b*]furan-2,8-dione).

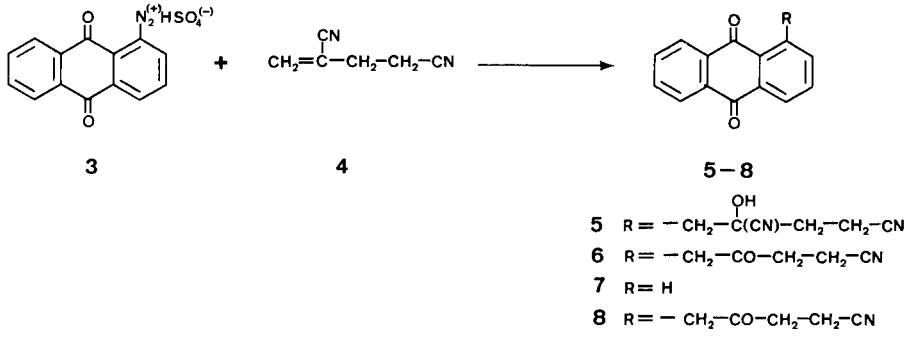
The diazotation of 1-aminoanthraquinone to anthraquinone diazonium hydrogensulfate (**3**) was performed essentially according to a known procedure [2a]. Generally, a slightly moist diazonium salt was used for the arylation reactions, but for some of the experiments the dry salt was required. This was obtained by washing the moist salt consecutively with ice water, methanol and finally with ether, yielding off-colored crystals which gave satisfactory analysis.

Addition of 2-methyleneglutaronitrile (**4**) to a suspension of **3** and copper(I) chloride in methanol resulted in the evolution of nitrogen and formation of the arylation product by vicinal addition of the 1-anthraquinone group and hydroxyl to the carbon-carbon double bond (Scheme 1). Gas chromatography of the crude reaction mixture indicated that it consisted of 72% of 3-hydroxy-4-(1-anthraquinone)-1,3-butandicarbonitrile (**5**), 1.2% of 3-oxo-4-(1-anthraquinone)butanecarbonitrile (**6**), and 20% of anthraquinone (**7**), the latter being attributed to the concurrently proceeding Sandmeyer reaction.

Anthraquinone (**7**) was extracted from the crude reaction mixture with cyclohexane to leave **5**. The structure of **5** was established by analytical and spectral data.

Essentially the same results were obtained using dry diazonium salt, except for a 6% lower yield of anthraquinone.

SCHEME 1



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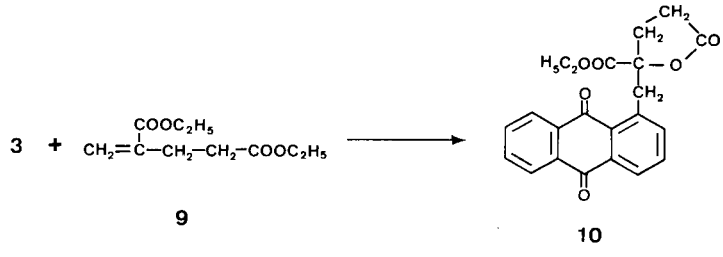

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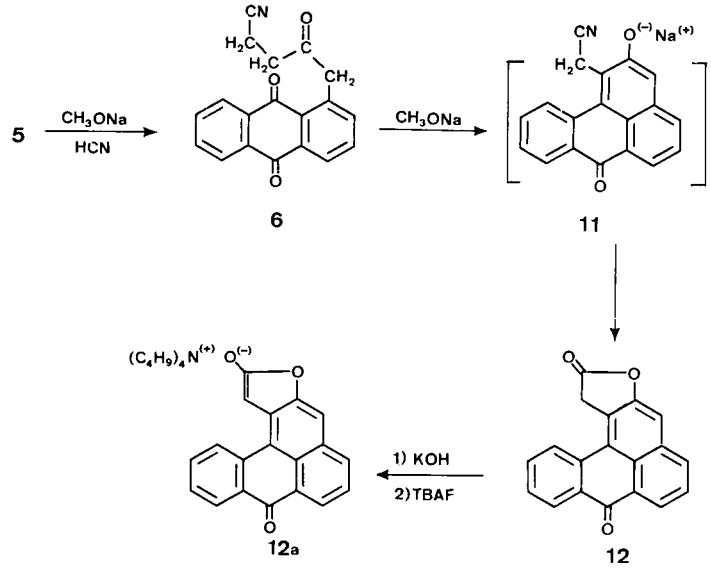


A slow evolution of hydrogen cyanide occurred even on heating **5** in ethanol yielding small amounts of ketone **6**. However, large quantities of **6** could be prepared by heating a solution of **5** in xylene in the presence of 10% of aluminum oxyde. This method provided ready access to the ketone **6** which was isolated in 98% yield.

Saponification of the nitrile group of **6** with sodium hydroxyde yielded the γ-ketocarboxylic acid **8**.

An entirely different reaction was observed when 2-methyleneglutaric acid ester was used in the Meerwein reaction instead of the nitrile. Application of essentially the same synthetic procedure to the reaction of **3** with 3-methyleneglutaric acid diethyl ester (**9**) yielded in 30% the lactone **10** (Scheme 2). The structure was established by analytical and spectral data. The infrared spectrum exhibited absorptions at 1790 cm^{-1} for the γ-lactone ring while the carbonyl freqeuncy of the ester group appears at 1740 cm^{-1}. The ^{13}C-nmr spectrum confirmed further this structural assignment.

Benzanthrone Lactone.

Addition of sodium methylate to a solution of **5** in dimethylformamide effected two consecutive ring closures and furnished 2-hydroxybenzanthrone-1-acetic acid lactone (**12**) in 91% yield (scheme 3).

Compound **12** was obtained in the form of dark yellow crystals which are sparingly soluble in dimethylformamide, pyridine or *N*-methylpyrrolidine. It exhibits an absorption band at 1821 cm^{-1} which is characteristic for unsaturated γ-lactones. The infrared spectra of substituted 2(3*H*)-benzofuranones show absorption in the region of 1818-1821 cm^{-1} [7]. Further proof of structure was obtained from the ^{13}C-nmr spectrum.

The lactone was also formed by treating **6** with a solution of sodium methylate in methanol. The reaction is envisaged as a base catalyzed condensation occurring between one keto group of the anthraquinone and a methylene group of the side chain, forming an intermediate salt **11**. Alkaline hydrolysis of the nitrile function of **11** takes place concurrently with formation of the γ-lactone ring to yield **12**.

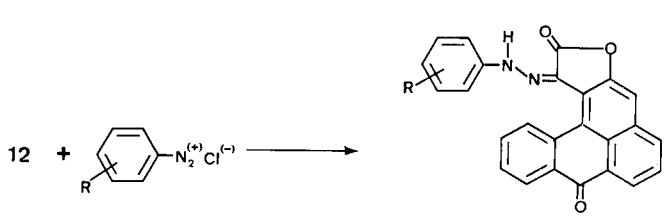
Addition of a solution of potassium methylate to a solution of **12** in dimethylsulfoxyde gave rise to formation of an intense blue solution, from which the potassium salt of the enol form of **12** was isolated as a violet amorphous material. Since it could not be obtained in analytical purity and the solutions in dimethylsulfoxyde exhibited only a poorly resolved nmr spectrum, we prepared the tetrabutylammonium salt **12a** by adding a large excess of tetrabutylammonium fluoride trihydrate (TBAF) to a solution of **12a** in dimethylformamide. Subsequent dilution with water caused precipitation of **12a** (Scheme 3). It was obtained from acetonitrile as dark blue crystals with a metallic copperlike surface. Solutions in polar organic solvents exhibit an intense blue colour.

The structure of **12a** could be inferred from the spectroscopic data. The infrared spectrum lacks most notably the characteristic absorption band of the γ-lactone carbonyl at 1821 cm^{-1}, while the absorption of the ketone band which belongs to the benzanthrone system appears at 1676 cm^{-1}.

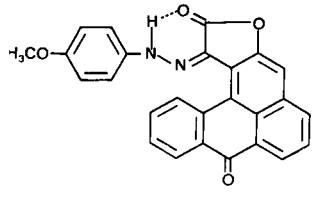
The ^1H and ^{13}C-nmr chemical shifts strongly support structure **12a**. Assignments for the protons are inferred in the ^1H spectrum by selective decoupling and NOE experiments. Irradiation at 5.56 ppm (H-8) cause a nuclear overhauser effect on the signal at 8.40 ppm. In the ^{13}C nmr spectrum all signals are separated, and partial assignments become feasible by a selective decoupling experiment at 7.36 ppm.

This appears to be the first case to our knowledge, in which a γ-lactone attached to an aromatic system fails to undergo the usual hydrolytic cleavage of the lactone function in alkaline medium, but rather forms an α-hydroxyfurane, and thus becomes part of the entire polycyclic system. The 2(3*H*)-benzofuran-2-one itself which might be considered as a built-in part of the entire structure of **12** does not show any indication of a similar enolization to yield isolable salts of 2-hydroxybenzofuran.

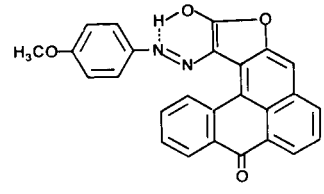
SCHEME 4



The methylene group of the lactone ring reacted readily with aromatic diazonium salts to furnish substituted arylhydrazone derivatives of the benzanthrone lactone **13-18** (Scheme 4). The analytical and spectral data are compiled in Tables 2 and 3. The structures could be inferred from the infrared and the nmr data. The infrared spectra exhibit characteristic bands at 1742 cm^{-1} for compounds **13-15**, **18**, and at 1722 cm^{-1} for **17**, respectively, which are characteristic of a substituted lactone ring [8a,b]. Generally, substitution of the lactone ring by the azo group shifted the frequency of the carbonyl band to lower frequencies by as much as 98 cm^{-1} for **13-15**, and 121 cm^{-1} for **17**, as compared with the unsubstituted lactone ring of **12**. They further show a band varying little in frequency between 1630 cm^{-1} and 1635 cm^{-1} attributable to the C=N group. ^1H and ^{13}C chemical shifts were recorded for the *p*-methoxy derivative **17** only, because of its fair solubility in deuteriochloroform, while the very low solubility of the other derivatives frustrated recordings of their nmr spectral data.



17



17a

The low field signal at $\delta = 9.38$ ($J = 1.5$ Hz) was assigned to the H-8 proton (deshielding by N=C), and all the other assignments rest on decoupling experiments. In the ^{13}C nmr spectrum only the signals of those carbon atoms could be observed which bear hydrogen atoms, because of the low solubility of **17**. The signals of the *p*-disubstituted substituent are in agreement with the proposed structure of a hydrazone, rather than the structure of an azo tautomer as pictured in **17a**.

The ultraviolet spectral data of **13-18** are compiled in Table II.

Table I

Formula **13-18**

Compound	R	Yield %	MP °C [a]	Molecular Formula	Analysis Calcd./Found C	H	Cl	N	S
13	H	82	269 dec	$C_{25}H_{14}N_2O_3$	76.92 76.90	3.62 3.65			
14	4-Cl	75	276-280 dec	$C_{25}H_{13}ClN_2O_3$	70.68 70.45	3.09 3.20	8.35 8.27	6.59 6.52	
15	4-NO_2	87	305-310 dec	$C_{25}H_{13}N_3O_5$	68.97 69.01	3.01 3.24		9.65 9.72	
16	4-SO_3Na	80	306-310 dec	$C_{25}H_{14}N_2O_6SNa$	63.82 63.59	3.00 3.10		5.95 5.92	6.81 6.80
17	4-OCH_3	71	266-268 dec	$C_{26}H_{16}N_2O_4$	74.28 74.18	3.84 3.76		6.67 6.58	
18	3,5-$(NO_2)_2$	64	300-305 dec	$C_{25}H_{12}N_4O_7$	62.51 62.54	2.52 2.70		11.66 11.59	

[a] Analytical samples were recrystallized from dimethylformamide.

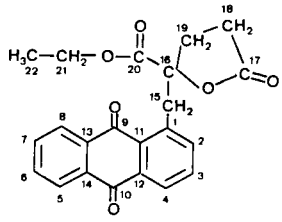
Table II

Ultraviolet Spectral Data of **13-18**

Compound	UV λ Max (log ε) [a]					
13				391 (23520)	482 (22680)	
14	290 (sh)	308 (sh)	364 (sh)	390 (18480)	482 (12040)	
15	282 (sh)	333 (11560)	370 (sh)	391 (32480)	477 (30920)	504 (sh)
16				394 (22360)	493 (21960)	
17		324 (sh)		401 (23440)		514 (24280)
18			364 (sh)	380 (23440)	461 (21480)	

[a] Measured in dimethylformamide solution.

Related structures of arylhydrazone compounds of 2,3-dioxotetrahydrofuran have been reported [9,10,11].



10

EXPERIMENTAL

Melting points were determined in open capillary tubes and are uncorrected. The ^1H- and the ^{13}C nmr spectra were recorded on a Bruker HX-360 nmr spectrometer in the fourier transform mode.

Samples for the infrared spectra were prepared in potassium bromide disks.

3-Hydroxy-4-(1-anthraquinone)-1,3-butanedicarbonitrile (**5**).

To 750 ml of concentrated sulfuric acid were added with stirring 85 g (1.23 moles) of sodium nitrite over a period of 40 minutes, and stirring continued for an additional 15 minutes until all the crystals had dissolved. Then the solution was heated to 50° and 250 g (1.12 moles) of 1-aminoanthraquinone were added within 1 hour and stirred for an additional one half hour. The resulting diazonium solution was poured onto 1750 g of crushed ice, crystals were filtered, and washed on a filter with 250 ml of ice water. The moist product was pressed as dry as possible and used further as such. The cake of 1-anthraquinone diazoniumhydrogensulfate was slurried in a mixture of 2 ℓ of methanol and 530 g (5 moles) of 2-methyleneglutaronitrile. The resulting suspension was heated to 40° and 4.0 g of copper(I) chloride were added in small portions over a period of 15 minutes. When the evolution of nitrogen had ceased, the solution was heated to 50-55° for 1.5 hours. Then the temperature was lowered to 10° and 37.5 g of anthraquinone filtered from the solution. The filtrate was concentrated in a rotary evaporator, crystals collected by filtration

and washed on the filter with 50 ml of cold methanol yielding 282 g of crude product. This was transferred to the thimble of a soxhlet and extracted with cyclohexane. Evaporation of the cyclohexane solution yielded 5 g of anthraquinone, and the residue in the thimble gave 267 g (72%) of **5**. Gas chromatography indicated that it consisted of 98% of **5** and 1.9% of anthraquinone. Small samples (1 g) were recrystallized from ethanol yielding tan crystals, mp 144-146°, ir: cm^{-1}; 3370 (OH), 2246 (CN), 1672, 1591, 1580, 1322, 1290, 1105, 965, 718.

Anal. Calcd. for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.47, H, 4.17; N, 8.16.

3-Oxo-4-(1-anthraquinone)butancarbonitrile (**6**).

A suspension of 8 g (0.024 mole) of **5** and 0.8 g of aluminum oxide (Woelm, neutral) in 50 ml of xylene was heated to reflux for a period of 40 minutes. The crystals went into solution as the reaction proceeded. Carbon black was added before filtration and the hot solution filtered from insoluble parts. The filtrate was evaporated to dryness and the crystalline residue recrystallized from toluene, yielding 5.9 g (82%) of light yellow crystals, mp 165-167°; ir: cm^{-1} 2245 (CN), 1710 (CO), 1672, 1590, 1580; ^{1}H-nmr (DMSO-d_6): δ 4.31 (anthraquinone-CH_2-CO), 3.09 (CH_2-CN), 2.64 (-CO-CH_2-).

Anal. Calcd. for $C_{19}H_{13}NO_3$: C, 75.24; H, 4.32; N, 4.62. Found: C, 75.18; H, 4.34.

γ-Oxo-4-(1-anthraquinone)butyric Acid (**8**).

A solution of 5 g (0.0165 mole) of **6** in 40 ml of concentrated sulfuric acid was stirred for a period of 2 hours. Then the solution was slowly added to 200 ml of ice water and stirred for 12 hours. The precipitate was filtered and washed with water, yielding 5.1 g (96%) of **8**. An analytical sample was prepared by recrystallization from methyl cellosolve and afforded yellow crystals, mp 195° dec; ir: cm^{-1} 1720 (COOH), 1660 (CO).

Anal. Calcd. for $C_{19}H_{14}O_5$: C, 70.80; H, 4.38. Found: C, 70.58; H, 4.47.

4-(1-Anthraquinonemethane)-4-carboxyethyl-4-butanolide (**10**).

To a slurry of anthraquinone diazoniumhydrogensulfate (0.5 mole) (prepared as above from 112 g of 1-aminoanthraquinone) in 1100 ml of methanol was added 233 g (1.15 moles) of 2-methyleneglutaric acid diethylester and heated to 55°. Nitrogen evolution commenced after the addition of copper(I) chloride in small portions. When the nitrogen evolution had subsided after 30 minutes, stirring was continued at 55° for an additional hour. The filtered solution was concentrated in a rotary evaporator and the almost dry residue added to 1 l of water. The aqueous layer was decanted from the semisolid residue and replaced by a mixture of 600 ml of petroleum ether and 100 ml of methanol, and stirred for 24 hours. Crystals of **10** were filtered and washed with 200 ml of petroluem ether. Recrystallization from 700 ml of ethyl cellosove yielded 56.8 g (30%) of yellow crystals which were further purified by recrystallization from 200 ml of chlorobenzene furnishing 47.1 g of analytically pure **10**, mp 163-164°; ir: cm^{-1} 1785 (lactone), 1742 (ethyl ester); ^{13}C-nmr (deuteriochloroform): δ 185.81 C-1, 183.13 C-2, 175.43 C-3, 171.27 C-4, 138.74

Formula **10** d7

C-5, 137.46 C-6, 135.32 C-7, 135.02 C-8, 134.28 C-9, 134.08 C-10, 133.83 C-11, 133.19 C-12, 132.74 C-13, 132.58 C-14, 127.56 C-15, 126.68 C-16, 86.48 C-17, 78.36 C-18, 77.08 C-19, 75.80 C-20, 62.27 C-21, 38.73 C-22.

Anal. Calcd. for $C_{24}H_{24}O_7$: C, 67.91; H, 5.70. Found: C, 68.20; H, 5.73.

1-*H*-Anthra[1,9-*ef*]benzo[*b*]furan-2,8-dione (**12**).

A. To a stirred solution of 16.5 g (0.05 mole) of **5**, in 100 ml of dimethylformamide were added 13.5 g (0.25 mole) of sodium methylate at such a rate that the temperature did not exceed 50°. Stirring was continued for another 45 minutes. The dark blue suspension was cooled and added to a solution of 50 ml of concentrated hydrochloric acid in 600 ml of water. The precipitate was filtered, washed with water and dried, yielding 13 g (91%) of **12**. A sample was recrystallized from *N*-methylpyrrolidine affording dark yellow crystals, mp 300° dec; ir: cm^{-1} 1814 (unsaturated lactone), 1640, 1602 (anthraquinone absorption bands); uv (methanol): λ max 284 (8850), 308 (6100), 362 (8700), 388 (8680); ms: M^+ m/e 286; nmr (DMSO-d_6): δ 8.59 (H-4), 8.44 (H-2), 8.44 (H-5), 8.30 (H-8), 8.02 (H-1), 7.94 (H-7), 7.90 (H-3), 7.73 (H-6), 4.73 (CH_2).

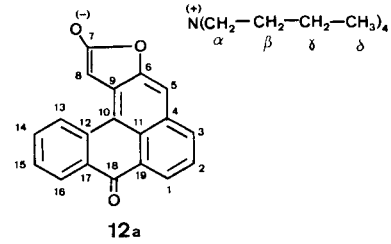
Anal. Calcd. for $C_{19}H_{10}O_3$: C, 79.71; H, 3.52. Found: C, 79.68; H, 3.56.

B. To a solution of 3.03 g (0.01 mole) of **6**, in 20 ml of dimethylformamide was added dropwise over a period of 5 minutes 8.94 g of a 30% solution of sodium methylate in methanol at a temperature of 40-50°, and maintained for half an hour. The blue suspension was added to a mixture of 100 ml of water and 10 ml of concentrated hydrochloric acid, and stirred for 1 hour. Crystals were filtered and washed with water yielding 2.8 g (98%) of **12**.

Tetrabutylammonium 8-Oxoanthra[1,9-*ef*]benzo[*b*]-2-furanolate (**12a**).

A suspension of 2.86 g (0.01 mole) of **12** in 200 ml of dimethylsulfoxide was heated to 160° to effect dissolution of crystals. Subsequently the temperature was lowered and 4.05 ml of a solution of potassium methylate in methanol (prepared by dissolving 1 g of potassium in 10 ml of methanol) added. It was stirred at 50° for 30 minutes, filtered through a glass fritted funnel under an atmosphere of nitrogen and then evaporated to dryness at 50-70°/1 torr. The purple residue was removed from the flask and freed of volatile products at 100°/1 torr. affording 3.3 g of crude potassium salt. To a solution of 2.6 g (0.1 mole) of this salt in 40 ml of dimethylformamide was added a solution of 8 g (0.025 mole) of tetrabutylammoniumfluoride trihydrate (TBAF) in 15 ml of the same solvent. The initial blue-red colour changed slowly to a deep blue. After 20 minutes the solution was added to a solution of 15 g of TBAF in 300 ml of water. The violet crystals were collected by filtration after standing for 24 hours, and dried at 80°/1 torr, yielding 2.68 g (52%) of product. Recrystallization from acetonitrile furnished violet crystals, mp 148-150° dec; ir: cm^{-1} 2920, 2860, 1676, 1616, 1530, 1495, 1470, 1330, 1302, 1270, 1062; uv (dimethylformamide): max 314 nm (ε 14580), 348 (ε 7640), 385 (ε 8200), 590 (ε 13400); nmr (DMSO-d_6): δ 8.45 (H-1, H-16), 8.40 (H-13), 8.00 (H-3), 7.75 (H-14), 7.36 (H-2, H-15), 7.26 (H-5), 5.56 (H-8), 3.07 (H-α), 1.50 (H-β), 1.25 (H-γ), 0.90 (H-δ); ^{13}C-nmr (DMSO-d_6): δ 180.72 (C-18), 171.51 (H-7), 151.25 (H-6), 141.33 (H-11), 138.50 (H-12), 132.75 (H-3), 131.77 (C-14), 128.73 (C-17), 127.66 (C-19), 128.88 (C-1), 126.20 (C-4), 125.73 (C-16), 125.00 (C-10), 124.67 (C-13), 122.71 (C-15), 119.75 (C-2), 103.24 (C-5), 101.69 (C-9), 77.62 (C-8), 57.49 (C-α), 22.93 (C-β), 19.04 (C-γ), 13.27 (C-δ).

Anal. Calcd. for $C_{35}H_{45}NO_3$: C, 79.65; H, 8.60; N, 2.65. Found: C, 79.48; H, 8.58; N, 2.71



12a

The general procedure for the synthesis of **13-18** is exemplified with the preparation of **17**.

1-(*p*-Methoxyphenylhydrazono)anthra[1,9-*ef*]benzo[*b*]furan-1,2,8-trione (**17**).

To a slurry of 2 g (0.007 mole) of **12** in 100 ml of dimethylformamide was added a freshly prepared aqueous solution of 0.01 mole of 4-methoxyphenyl diazoniumchloride and stirred for 24 hours. Dark red crystals were filtered from the solution and washed successively with dimethylformamide and methanol, affording 2.7 g of **17**. Recrystallization from dimethylformamide yielded red crystals; ^{1}H-nmr (deuteriochloroform): δ 12.96 (NH), 3.86 (OCH_3), 9.38 (C-8), 7.75 (C-7), 7.65 (C-6), 8.54 (C-5), 8.69 (C-4), 7.75 (C-3), 8.14 (C-2), 7.67 (C-1), $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 7.5 Hz, $J_{2,4}$ = 1.5 Hz, $J_{5,6}$ = 7.5 Hz, $J_{6,7}$ = 7.5 Hz, $J_{7,8}$ = 8.0 Hz, $J_{5,7}$ = 1.5 Hz;

^{13}C-nmr (deuteriochloroform): δ 134.42 (C-2), 132.08 (C-7), 129.36 (C-3) 129.02 (C-4), 127.62 (2x) (C-5,C-6), 126.92 (C-8), 116.63 (C-9), 115.20 (C-10), 108.97 (C-1), 55.63 (OCH_3).

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