SOME FURTHER 2-(4-SUBSTITUTED 1-PIPERAZINYL)ACETAMIDES DERIVED FROM 6,11-DIHYDRODIBENZO[*b*, *e*]THIEPIN. TRANSFORMATIONS OF 6,11-DIHYDRODIBENZO[*b*, *e*]THIEPIN DERIVATIVES INTO ANTHRAQUINONES, ANTHRONES AND ANTHRACENES

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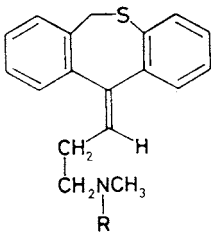
Reactions of the secondary amines *I* and *VIII* with chloroacetyl chloride gave the 2-chloroacetamides *II* and *IX* affording by substitution reactions with 1-methylpiperazine, 2-(1-piperazinyl)ethanol and 3-(1-piperazinyl)propanol the title compounds *III*—*V* and *X*—*XII*. The starting amine *VIII* was prepared from the ketone *XIV* via *XVII* and *VII*. The product of 1,6-addition and the following dehydrogenation *XVIII* was obtained as a by-product of the reaction of *XIV* with 1-methyl-4-piperidylmagnesium chloride. Reaction of 2-fluorodibenzo[*b*,*e*]thiepin-11(6*H*)-one (*XV*) with sodium hydride in dimethylformamide and the following hydrolysis gave 2-fluoroanthraquinone (*XXVII*). An attempt at trapping the presumed dianion of the type B by treatment with methyl iodide and the following hydrolysis resulted in a mixture of *XXVII* and the anthracenes *XXXI* and *XXXII*. A similar reaction sequence starting from the ketone *XIV* gave the anthrones *XXX* and *XXXIV*, 9-methoxy-10-(methylthio)anthracene (*XXXIII*) (main product) and anthraquinone (*XXVIII*). Oxidation of *XXXIII* with *m*-chloroperbenzoic acid or hydrogen peroxide gave either the sulfone *XXXV* or *XXXVI*.

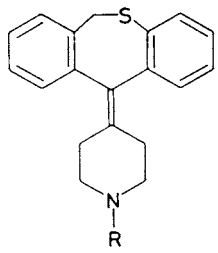
In a previous communication[1] we used 6,11-dihydrodibenzo[*b*,*e*]thiepin-11-amine and (6,11-dihydrodibenzo[*b*,*e*]thiepin-11-yl)methylamine for preparing the N-(chloroacetyl) derivatives which, in turn, were processed by substitution reactions with 1-substituted piperazines to the corresponding 2-(4-substituted 1-piperazinyl)-acetamides exhibiting useful pharmacodynamic properties (local anaesthetic, anti-arrhythmic, anti-ulcer). The first part of this paper represents a continuation in the mentioned line.

The first amine to be used in the mentioned sequence was (*E*)-N-methyl-3-(6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ylidene)propylamine (northiadene, *I*) (ref.[2]). Its reaction with chloroacetyl chloride in benzene in the presence of N,N-dimethylacetamide (for the method, cf. ref.[3]) gave the oily 2-chloroacetamide *II* which was subjected to substitution reactions with 1-methylpiperazine, 2-(1-piperazinyl)ethanol, and 3-(1-piperazinyl)propanol[4] in chloroform at 50—61°C. The obtained piperazine

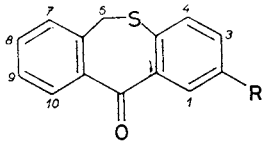
derivatives *III* – *V* were mostly oils giving crystalline salts with maleic acid; they were characterized by the mass, IR and ^{1}H NMR spectra. The second secondary amine which was chosen as the starting material was *VIII*, unknown until present. It was prepared from the ketone *XIV* (refs[5,6]) which was first reacted with 1-methyl-4-piperidylmagnesium chloride in tetrahydrofuran (cf. refs[7,8]) to obtain the crude *XVII*. Its chromatography on silica gel separated a compound $C_{20}H_{21}NOS$ (mass



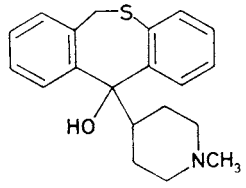
I, R = H
II, R = $COCH_2Cl$
III, R = $COCH_2N$◯NCH_3
IV, R = $COCH_2N$◯NCH_2CH_2OH
V, R = $COCH_2N$◯$N(CH_2)_3OH$



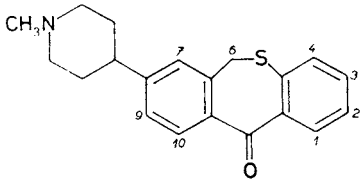
VI, R = CH_3
VII, R = $COOC_2H_5$
VIII, R = H
IX, R = $COCH_2Cl$
X, R = $COCH_2N$◯NCH_3
XI, R = $COCH_2N$◯NCH_2CH_2OH
XII, R = $COCH_2N$◯$N(CH_2)_3OH$



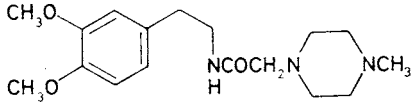
XIII
XIV, R = H
XV, R = F
XVI, R = OCH_3



XVII



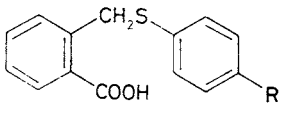
XVIII



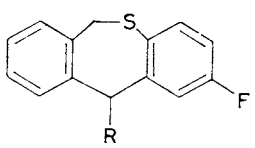
XIX

spectrum and elemental analysis) which was identified by spectra as *XVIII*. We are dealing here with the another product of 1,6-addition and the following spontaneous dehydrogenation (cf. refs[9,10]), observed by our team in some similar cases[11,12]. Dehydration of the crude *XVII* by refluxing with dilute sulfuric acid gave a mixture of *VI* and *XVIII* which was also separated by chromatography on silica gel. The less polar *VI* (ref.[7]) was obtained in the yield of 68% and the minor 1,6-addition product *XVIII* in the yield of 11%. Reaction of *VI* with ethyl chloroformate in boiling benzene (method, cf. ref.[2]) gave the oily carbamate *VII* which was purified by chromatography and characterized by spectra. Its hydrolysis with a concentrated solution of potassium hydroxide in ethanol (method, cf. ref.[2]) gave the crystalline amine *VIII* which was treated with chloroacetyl chloride in benzene in the presence of N,N-dimethylacetamide. The crystalline *IX* was treated similarly as *II* with 1-methylpiperazine, 2-(1-piperazinyl)ethanol and 3-(1-piperazinyl)propanol[4] in boiling chloroform. The obtained bases *X* (crystalline) and *XI* and *XII* (oils) wre characterized partly by spectra and transformed to crystalline salts with maleic acid. In the same connection N-(2-(3,4-dimethoxyphenyl)ethyl)-2-chloroacetamide[13,14], was transformed by treatment with 1-methylpiperazine under similar conditions to *XIX*.

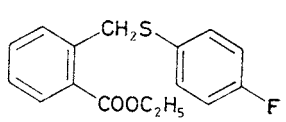
For further work we wanted to use as intermediate the hitherto undescribed 2-(isopropoxy)dibenzo[*b*,*e*]thiepin-11(6*H*)-one (*XIII*, R = $OCH(CH_3)_2$). It was described[5,6,15] that whereas acid of the general formula *XX* having as R atom of hydrogen or halogen (e.g. *XXI*, *XXII*) cyclized in high yields to ketones *XIII* (e.g. *XIV* or *XV*) by heating with polyphosphoric acid to 100–140°C, the methoxy acid *XXIII* is cleaved under these conditions and the cyclization to *XVI* has to be done in toluene[16], i.e. at a temperature limited by the boiling point of this solvent. In this situation we considered unlikely that the (isopropoxy) ketone (*XIII*, R = $OCH.(CH_3)_2$) could be prepared via the acid *XX* (R = $OCH(CH_3)_2$) and, therefore, we looked after a different possibility. The first attempt chosen was to try the nucleophilic displacement of the fluorine atom in some accessible intermediate (e.g. *XV* (refs[5,15])) by the isopropoxy group by treatment with sodium hydride and 2-propanol in dimethylformamide (similar conditions were repeatedly and successfully used by our team[17–21] in intramolecular reactions of *o*-fluorosubstituted sulfides). The ketone *XV* was prepared by cyclization of the acid *XXII* by heating with poly-



XX
XXI, R = H
XXII, R = F
XXIII, R = OCH_3



XXIV, R = OH
XXV, R = Cl

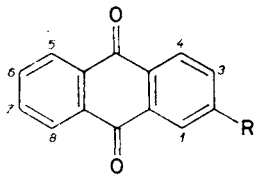


XXVI

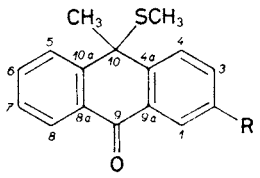
phosphoric acid to 140°C (refs[5,15]). Compound *XV* was reduced with sodium borohydride in ethanol to *XXIV* which was transformed to *XXV* by treatment with hydrogen chloride in benzene. The acid *XXII* (refs[5,15]) was esterified to *XXVI* by refluxing with ethanol and hydrogen chloride. From the reaction of *XXVI* with sodium hydride and 2-propanol in dimethylformamide at 65–70°C a single crystalline product was isolated and was identified by IR spectrum and analysis as the acid *XXII* (the considerably lower melting point in comparison with the literature[5,15] value has to be explained by the existence of a crystal modification).

Reaction of *XV* with sodium hydride and 2-propanol in dimethylformamide at 70°C, the following hydrolysis and chromatography of the mixture obtained resulted in a single crystalline product $C_{14}H_7FO_2$ (mass spectrum and elemental analysis) which was identified as 2-fluoroanthraquinone (*XXVII*) (ref.[22]). Because it was clear that the atom of fluorine did not participate in the reaction, the same reaction was repeated in the absence of 2-propanol. The result was the same: *XXVII* was obtained in a fair yield (56%). As the first step of transformation of *XV* to *XXVII* we suggest the formation of the monoanion *A* (R = F) which is produced by a partial sulfur extrusion which is analogical to the Wittig rearrangement (cf. refs[23–26]). Further treatment of anion *A* with sodium hydride leads to the unstable dianion *B* (R = F) which is hydrolyzed and oxidized to *XXVII* and hydrogen sulfide under complete sulfur extrusion. The logical idea was to try to trap this dianion by methylation with methyl iodide (cf. ref.[27]) because compound *XXIX* would be an interesting intermediate in the synthesis of new psychotropic agents. The ketone *XV* was thus reacted with excessive sodium hydride in dimethylformamide and the mixture was treated with excessive methyl iodide. After hydrolysis, the mixture was separated by flash chromatography on silica gel. Three homogeneous products were isolated but none of them was the desired *XXIX*. The first product formed yellowish needles and melted at 121·5–122·5°C. Its composition $C_{16}H_{13}FOS$ was determined by combination of elemental analysis and mass spectrum; UV, IR, ^{1}H NMR, and ^{13}C NMR spectra led to the assignment of the structure of 2-fluoro-9-methoxy-10-(methylthio)anthracene (*XXXI*). The unstable dianion *B* (R = F) evidently was transformed to the more stable dianion *C* (R = F) which was than trapped. *XXXI* is the main product of the reaction (26%). In the chromatographic sequence it was followed by *XXVII*. The last product to be eluted was a compound $C_{17}H_{16}O_2S$ showing again the anthracene chromophore and was identified as *XXXII*. It is the product of the nucleophilic displacement of the fluoride anion by the methoxide anion.

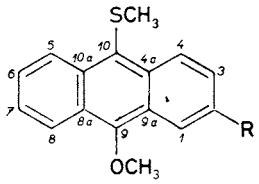
With the exception of the minor product *XXXII*, the fluorine atom did not participate in the reaction. The following experiment, including the treatment with sodium hydride followed by methyl iodide, was, therefore, carried out in the nonfluorinated series, i.e. it started from *XIV* (refs[5,6]). It gave two products which were separated by crystallization and chromatography of the mixture obtained. The first (16%) was a yellowish compound $C_{16}H_{14}OS$ (elemental analysis and mass spectrum)



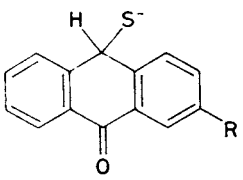
XXVII, R = F
XXVIII, R = H



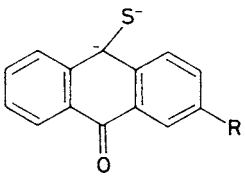
XXIX, R = F
XXX, R = H



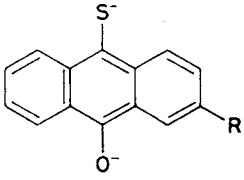
XXXI, R = F
XXXII, R = OCH_3
XXXIII, R = H



A



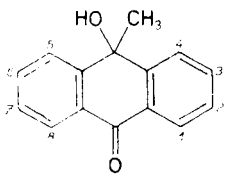
B



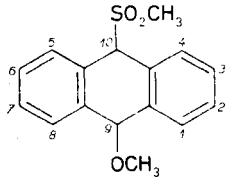
C

which was considered to be *XXX*. It, however, did not react with 2,4-dinitrophenylhydrazine, semicarbazide, and 1-methyl-4-piperidylmagnesium chloride[7] and was not reduced with sodium borohydride or lithium aluminium hydride. A more detailed investigation of the spectra identified the product as 9-methoxy-10-(methylthio)anthracene (*XXXIII*). The transformation of the dianion *B* (R = H) to the dianion *C* (R = H) was thus again involved. The second product (29%) was the colourless $C_{15}H_{12}O_2$, identified as the known 10-hydroxy-10-methylanthrone (*XXXIV*) (refs[28,29]), which is the product of preferential C-methylation of the dianion *B* (R = H) and the following hydrolysis with the complete extrusion of sulfur. A further similar experiment, carried out slightly differently (the mixture of *XIV*, sodium hydride, and dimethylformamide was warmed to 40–45°C and methyl iodide was added in two portions) gave a mixture of three products which were separated by chromatography on silica gel. The first to be eluted with benzene was *XXXIII* (50%) which was followed by a colourless isomer (18%) $C_{16}H_{14}OS$, this time really 10-methyl-10-(methylthio)anthrone (*XXX*) (the band of Ar_2CO at 1 659 cm^{-1} in the IR spectrum and in the ^1H NMR spectrum signals of the C—CH_3 and S—CH_3 groups at δ 1·40 and 2·00, respectively). The immediate precursor of this compound is probably the assumed unstable dianion *B* (R = H). The last compound to be eluted was identified as anthraquinone (*XXVIII*) (13%), melting (242·5–244°C), however, distinctly lower in comparison with the highest literature[30,31] value (285–286°C). In general, the proceeding of our reactions is rather similar to that described by Ackrell[32] who started from methyl 11-oxo-6,11-dihydro-

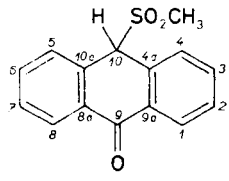
dibenzo[*b*,*e*]thiepin-3-carboxylate. Compound *XXXIII* was oxidized with the aim at obtaining the corresponding sulfoxide and sulfone. Reaction of *XXXIII* with a slight excess of hydrogen peroxide in a mixture of acetic acid and benzene at room temperature gave directly the compound $C_{16}H_{14}O_3S$, i.e. the sulfone *XXXV*. A similar reaction with a large excess of hydrogen peroxide in refluxing acetic acid afforded non completely homogeneous *XXVIII* (76%). Oxidation of *XXXIII* with *m*-chloroperbenzoic acid gave 71% of *XXXV*. On the other hand, the oxidation of *XXXIII* with 9 equivalents of hydrogen peroxide in boiling acetic acid gave in addition to anthraquinone (*XXVIII*) (57%) a further sulfone $C_{15}H_{12}O_3S$ (32%), to which the structure *XXXVI* was attributed (the band of Ar_2CO at 1 664 cm^{-1} in the IR spectrum, the bands of SO_2 at 1 203 and 1 316 cm^{-1}; in the ^1H NMR spectrum the singlet of H-10 at δ 6·20; ^{13}C NMR spectrum in full agreement). Its formation from *XXXIII* or *XXXV* presumes first the cleavage of the 9-OCH_3 group which is then followed by transfer of the OH hydrogen to C-10.



XXXIV



XXXV



XXXVI

EXPERIMENTAL

The melting points of analytical samples were determined in the Kofler block (are not corrected); the samples were dried in vacuo of about 60 Pa over P_2O_5 at room temperature or at a suitably elevated temperature. UV spectra (mostly in methanol, λ_{max} in nm (log ε)) were recorded with a Unicam SP 8 000 spectrophotometer, IR spectra (mostly in Nujol, ν in cm^{-1}) with a Perkin–Elmer 298 or a Shimadzu IR-435 spectrophotometers, NMR spectra (in $CDCl_3$ unless stated otherwise, δ, J in Hz) with the CW-NMR spectrometer Tesla BS 487C (^1H at 80 MHz), FT NMR spectrometer Tesla BS 567A (^1H at 100 MHz; ^{13}C at 25·14 MHz), and FT NMR spectrometer Varian XL-200 (^1H at 200 MHz; ^{13}C at 50·3 MHz), and the mass spectra with Varian MAT 44S (GC-MS) spectrometer (*m*/*z* and %). The homogeneity of the products and composition of the mixtures were checked by thin-layer chromatography (TLC) on silica gel (Silufol). The extracts were dried with $MgSO_4$, Na_2SO_4 or K_2CO_3 and evaporated under reduced pressure on a rotating evaporator.

8-(1-Methyl-4-piperidyl)dibenzo[*b*, *e*]thiepin-11(6*H*)-one (*XVIII*)

A) Grignard reagent was prepared from 11·75 g 4-chloro-1-methylpiperidine and 2·15 g Mg in 100 ml tetrahydrofuran[7], and the stirred solution was treated with 10·0 g *XIV* (refs[5,6]) in 40 ml tetrahydrofuran, added eropwise over 20 min at 10–15°C, and the mixture was allowed to stand overnight at room temperature. It was poured to 90 g ice, 60 ml water and 22 g tartaric

acid, washed with benzene, made alkaline with NH_4OH, and extracted with chloroform. Processing of the extract gave 14·0 g crude *XVII* which could not be purified by crystallization. It was divided to two equal parts which were processed separately.

The crude product (7·0 g) was chromatographed on a column of 120 g silica gel. Elution with a mixture of 90% of chloroform, 5% of methanol, and 5% of chloroform saturated with NH_3 gave 0·94 g (13%) of *XVIII*, m.p. 204·5—207°C (benzene). Mass spectrum: 323 (M^+, $C_{20}H_{21}NOS$, 46), 322 (17), 145 (3), 97 (32), 83 (17), 78 (13), 70 (100), 57 (20), 44 (24), 43 (52), 42 (40). UV spectrum: 237·5 (4·40), infl. 266 (3·86), infl. 350 (2·46). IR spectrum: 736, 840, 900 (4 and 2 adjacent Ar–H); 1 276 (C–O); 1 583, 1 601, 3 045 (Ar), 1 623 (Ar_2CO), 2 678, 2 738, 2 760, 2 780 ($N–CH_3$). ^1H NMR spectrum (100 MHz): 1·80—3·00 m, 9 H (4 CH_2 and CH of piperidine); 2·34 s, 3 H ($N–CH_3$); 4·04 s, 2 H (2 H-6); 7·08—7·40 m, 5 H (H-2, H-3, H-4, H-7, H-9); 7·60 bd, 1 H (H-10); 8·23 m, 1 H (H-1). For $C_{20}H_{21}NOS$ (323·5) calculated: 74·27% C, 6·54% H, 4·33% N, 9·91% S; found: 74·52% C, 6·73% H, 4·31% N, 10·01% S.

Continued elution with the same mixture afforded 5·10 g (71%) of 11-(1-methyl-4-piperidyl)-6,11-dihydrodibenzo[*b*, *e*]thiepin-11-ol (*XVII*), m.p. 185—187°C. Ref.[7], m.p. 186—186·5°C.

B) The second part of the crude product of the Grignard reaction (7·0 g) was refluxed for 30 min with a solution of 14·9 g H_2SO_4 in 70 ml water. After cooling it was made alkaline with 30 ml NH_4OH and extracted with chloroform. The extract was washed with water and processed. The residue after its evaporation (7·5 g) was chromatographed on 50 g silica gel. Elution with a mixture of 93% of chloroform, 5% of chloroform saturated with NH_3, and 2% of methanol gave 4·65 g (68%) of 11-(1-methyl-4-piperidylidene)-6,11-dihydrodibenzo[*b*,*e*]thiepin (*VI*). It gave the hydrochloride melting at 268—270°C (ethanol–ether). Ref.[7], m.p. 267—272°C.

Continued elution with the same mixture gave 0·83 g (12%) of *XVIII*, m.p. 204—207°C (benzene), identical with product obtained under *A*).

11-(1-Ethoxycarbonyl-4-piperidylidene)-6,11-dihydrodibenzo[*b*,*e*]thiepin (*VII*)

A solution of 5·00 g *VI* in 25 ml benzene was added to a stirred solution of 3·53 g ethyl chloroformate in 35 ml benzene at 75°C. The mixture was refluxed for 2·5 h, after cooling washed with diluted hydrochloric acid and water, dried, and evaporated; 6·04 g oil which was dissolved in 25 ml benzene and the solution was filtered through a column of 15 g silica gel. The column was washed with 400 ml of benzene and the solution was evaporated; 5·05 g (85%) of rather homogeneous *VII*. Mass spectrum: 365 (M^+, $C_{22}H_{23}NO_2S$, 34), 336 (4), 332 (5), 320 (3), 292 (6), 243 (28), 235 (29), 234 (29), 215 (44), 202 (31), 178 (35), 154 (100), 116 (31), 56 (49), 42 (83). IR spectrum (KBr): 731 (4 adjacent Ar–H); 1 227 (C–O); 1 554, 1 563, 1 584 (Ar); 1 687 (NCOOR). ^1H NMR spectrum (80 MHz): 1·19 t, 3 H ($C–CH_3$); 2·08 bt, 2 H (H-3 and H-5 of piperidine, $J = 6·0$); 2·39 bt, 2 H (H-3 and H-5 of piperidine, $J = 6·0$); 3·00—3·90 bm, 4 H (CH_2NCH_2 of piperidine); 4·06 q, 2 H (OCH_2, $J = 7·0$); 4·10 ABq, 2 H ($ArCH_2S$, $J = 13·3$); 7·05 m, 8 H (ArH). For $C_{22}H_{23}NO_2S$ (365·5) calculated: 3·83% N, 8·77% S; found: 3·43% N, 8·38% S.

11-(4-Piperidylidene)-6,11-dihydrodibenzo[*b*,*e*]thiepin (*VIII*)

A mixture of 4·47 g *VII*, 3·43 g KOH and 30 ml ethanol was stirred and refluxed for 2 h. After partial cooling the mixture was diluted with 50 ml water and extracted with benzene. Processing of the extract gave 2·58 g (72%) of *VIII*, m.p. 91—94°C (benzene–ether). Mass spectrum: 293 (M^+, $C_{19}H_{19}NS$, 40), 250 (100), 218 (23), 217 (23), 203 (20), 202 (20), 178 (10), 82 (18), 56 (67), 44 (34), 42 (78). IR spectrum (KBr): 761 (4 adjacent Ar–H); 1 481, 1 553, 1 583 (Ar). ^1H NMR spectrum (80 MHz): 1·58 bs, 1 H (NH); 2·06 bt, 2 H (H-3 and H-5 of piperidine, $J = 5·5$); 2·38 bt, 2 H (H-3 and H-5 of piperidine, $J = 5·5$); 2·85 bm, 4 H (CH_2NCH_2 of piperidine);

4·12 ABq, 2 H ($ArCH_2S$, J = 13·3); 7·10 m, 8 H (ArH). For $C_{19}H_{19}NS$ (293·4) calculated: 77·77% C, 6·53% H, 4·77% N, 10·93% S; found: 77·70% C, 6·73% H, 4·66% N, 10·92% S.

(*E*)-N-Methyl-N-(3-(6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ylidene)propyl)-2-chloroacetamide (*II*)

A stirred solution of 4·42 g *I* (ref.[2]) in 30 ml benzene was treated with 1·99 g N,N-dimethylacetamide and then with a solution of 2·58 g chloroacetyl chloride in 20 ml benzene, added dropwise over 10 min. The mixture was stirred for 30 min at room temperature and for 1·5 h at 40°C, diluted with 50 ml chloroform, washed with water, dried, and evaporated; 5·01 g (89%) of almost homogeneous oily *II*. UV spectrum: 228 (4·38), infl. 263 (3·89), 302 (3·35). IR spectrum (CS_2): 729, 747, 761 (indicates the retained (*E*)-configuration, 4 adjacent Ar–H); 1 655 (NCOR); 3 015, 3 075 (Ar). For $C_{20}H_{20}ClNOS$ (357·9) calculated: 9·91% Cl, 3·91% N, 8·96% S; found: 10·00% Cl, 3·75% N, 9·23% S.

11-(1-(2-Chloroacetyl)-4-piperidylidene)-6,11-dihydrodibenzo[*b*,*e*]thiepin (*IX*)

A solution of 1·50 g *VIII* and 0·62 g N,N-dimethylacetamide in 20 ml benzene was stirred and treated with a solution of 0·81 g chloroacetyl chloride in 20 ml benzene, and the mixture was refluxed for 1·5 h. After cooling it was diluted with 60 ml chloroform, the solution was washed with water and processed. The crude oily product (1·9 g) crystallized slowly from benzene; 1·51 g (80%), m.p. 145–147°C. Mass spectrum: 369 (M^+, $C_{21}H_{20}ClNOS$), 336, 333. IR spectrum (KBr): 762 (4 adjacent Ar–H); 1 235 (C–O); 1 647 (CONRR'). ^{1}H NMR spectrum (80 MHz): 2·12 bt, 2 H (H-3, H-5 of piperidine, J = 5·75); 2·48 bt, 2 H (H-3, H-5 of piperidine, J = 5·75); 2·90–3·90 bm, 4 H (CH_2NCH_2 of piperidine); 4·00 s, 2 H ($COCH_2Cl$); 4·10 ABq, 2 H ($ArCH_2S$, J = 13·3); 7·10 m, 8 H (ArH). For $C_{21}H_{20}ClNOS$ (369·9) calculated: 68·19% C, 5·45% H, 9·58% Cl, 3·79% N; 8·67% S; found: 67·77% C, 5·62% H, 9·19% Cl, 3·73% N, 8·69% S.

(*E*)-N-Methyl-N-(3-(6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ylidene)propyl)-2-(4-methyl-1-piperazinyl)acetamide (*III*)

A mixture of 2·46 g 1-methylpiperazine, 40 ml chloroform and 4·00 g *II* was refluxed for 2 h, diluted with 20 ml chloroform, washed with water, dried, and evaporated. The oily residue crystallized from a mixture of benzene and light petroleum; 4·18 g (89%) of *III*, m.p. 116–119°C (hexane). Mass spectrum: 421 (M^+, $C_{25}H_{31}N_3OS$, 3); 388 (2), 365 (2·5), 351 (3), 338 (2), 250 (3), 217 (4), 113 (100), 99 (8), 98 (7), 70 (66), 44 (18), 42 (20). IR spectrum (KBr): 766 (4 adjacent Ar–H); 1 485 (Ar); 1 637 (CONRR'); 2 798 (N–CH_3). ^{1}H NMR spectrum (80 MHz): 1·80 to 3·70 and 4·40–5·00 2 m, 22 H (2 NCH_3, 6 NCH_2, C–CH_2–C and $ArCH_2S$); 5·85 bt, 1 H (=CH, J = 7·5); 6·88–7·30 bm, 8 H (ArH). For $C_{25}H_{31}N_3OS$ (421·6) calculated: 71·22% C, 7·41% H, 9·97% N, 7·60% S; found: 71·48% C, 7·52% H, 9·76% N, 7·68% S.

Bis(*hydrogen maleate*), m.p. 148–152°C (ethanol). For $C_{33}H_{39}N_3O_9S$ (653·8) calculated: 60·63% C, 6·01% H, 6·43% N, 4·90% S; found: 60·40% C, 6·08% H, 6·36% N, 5·17% S.

(*E*)-N-Methyl-N-(3-(6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ylidene)propyl)-2-(4-(2-hydroxyethyl)-1-piperazinyl)acetamide (*IV*)

A similar reaction of 6·00 g *II* and 6·55 g 2-(1-piperazinyl)ethanol in 60 ml refluxing chloroform (1 h) gave 7·5 g (almost theoretical) of crude oily *IV* which was transformed to bis(hydrogen maleate), crystallizing from aqueous ethanol as monohydrate, m.p. 104–106°C. For $C_{34}H_{41}N_3O_{10}S + H_2O$ (701·8) calculated: 58·19% C, 6·18% H, 5·99% N, 4·57% S; found: 58·35% C, 5·95% H, 6·05% N, 4·78% S.

A sample of this salt was decomposed with NH_4OH and the released base was isolated by extraction with chloroform. Careful evaporation of the solvent in vacuo gave the purified oily *IV* which was used for recording the spectra. Mass spectrum: 451 (M^+, $C_{26}H_{33}N_3O_2S$, 0·4), 433 (0·3), 420 (0·8), 419 (0·8), 418 (0·8), 365 (1·3), 351 (2), 143 (100), 70 (38). IR spectrum (KBr): 751 (4 adjacent Ar–H); 1 067 (CH_2OH); 1 485, 1 554, 1 585 (Ar); 1 636 (CONRR'); 2 814 (N–CH_3); 3 396 (OH). ^{1}H NMR spectrum (80 MHz): 2·40 and 3·50 2 m, 17 H (=CCH_2CH_2N, $N(CH_2CH_2)_2NCH_2CH_2OH$); 2·80 s, 3 H (NCH_3); 3·02 bd, 2 H ($COCH_2N$, $J = 5·5$); 4·10 ABq, 2 H ($ArCH_2S$, $J = 13·3$); 5·85 bt, 1 H (=CH, $J = 7·5$); 7·10 m, 8 H (ArH).

(*E*)-N-Methyl-N-(3-(6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ylidene)propyl)-2-(4-(3-hydroxypropyl)-1-piperazinyl)acetamide (*V*)

A similar reaction of 5·00 g *II* with 6·04 g 3-(1-piperazinyl)propanol[4] in 60 ml of refluxing chloroform (1 h) gave 6·50 g of crude oily *V* which was transformed to the bis(hydrogen maleate) (8·83 g, 91%), m.p. 127–131°C (ethanol). Mass spectrum: 465 (M^+, $C_{27}H_{35}N_3O_2S$, 1), 432 (2), 365 (2), 351 (3), 331 (1·5), 250 (3·5), 217 (7), 157 (60), 127 (100), 98 (20), 84 (13), 70 (60). For $C_{35}H_{43}N_3O_{10}S$ (697·8) calculated: 60·24% C, 6·21% H, 6·02% N, 4·59% S; found: 59·88% C, 6·38% H, 6·12% N, 4·85% S.

A sample of this salt was decomposed with NH_4OH, the released base was isolated by extraction with chloroform, and the oily base (0·60 g) was purified by chromatography on 10 g silica gel. Elution with chloroform, saturated with NH_3, gave 0·52 g of the purified base which proved homogeneous (TLC). For $C_{27}H_{35}N_3O_2S$ (465·7) calculated: 69·64% C, 7·58% H, 9·02% N, 6·88% S; found: 69·62% C, 7·67% H, 8·84% N, 6·76% S.

11-(1-(2-(4-Methyl-1-piperazinyl)acetyl)-4-piperidylidene)-6,11-dihydrodibenzo[*b*,*e*]thiepin (*X*)

A similar reaction of 2·50 g *IX* with 1·5 g 1-methylpiperazine in 40 ml refluxing chloroform (2·5 h) gave 2·42 g (83%) of *X*, m.p. 152–155°C (benzene). IR spectrum: 730, 748, 759 (4 adjacent Ar–H); 1 477, 1 554, 1 581, 3 048 (Ar); 1 643 (CONRR'); 2 740, 2 760, 2 770 (N–CH_3). ^{1}H NMR spectrum (100 MHz): 2·28 s, 3 H (NCH_3); 2·50 bm, 12 H (2 H-3 and 2 H-5 of piperidine and $N(CH_2CH_2)_2N$); 3·20 bs, 2 H ($COCH_2N$); 3·00–4·00 bm, 4 H (CH_2NCH_2 of piperidine); 3·44 and 4·90 ABq, 2 H ($ArCH_2S$, $J = 13·0$); 7·00–7·40 m, 8 H (ArH). For $C_{26}H_{31}N_3OS$ (433·6) calcuated: 72·02% C, 7·21% H, 9·69% N, 7·39% S; found: 71·62% C, 7·44% H, 9·72% N, 7·47% S.

Bis(*hydrogen maleate*), m.p. 161–164°C (aqueous ethanol). For $C_{34}H_{39}N_3O_9S$ (665·8) calculated: 61·34% C, 5·90% H, 6·31% N, 4·82% S; found: 61·32% C, 6·08% H, 6·44% N, 5·15% S.

11-(1-(2-(4-(2-Hydroxyethyl)-1-piperazinyl)acetyl)-4-piperidylidene)-6,11-dihydrodibenzo[*b*,*e*]thiepin (*XI*)

A similar reaction of 2·50 g *IX* with 1·94 g 2-(1-piperazinyl)ethanol in 40 ml refluxing chloroform (3 h) gave 3·10 g of crude oily *XI*, which was transformed to bis(hydrogen maleate) (4·20 g, 89%), m.p. 151–154°C (ethanol). Mass spectrum: 463 (M^+, $C_{27}H_{33}N_3O_2S$, 0·9), 445 (1), 432 (0·9), 377 (2·5), 363 (4), 318 (15), 143 (100), 70 (59), 56 (55), 44 (54), 42 (82). For $C_{35}H_{41}N_3O_{10}S$ (695·8) calculated: 60·42% C, 5·94% H, 6·04% N; 4·61% S; found: 60·03% C, 6·05% H, 5·92% N, 4·63% S.

A sample of this salt was decomposed with 10% NaOH and the released base was isolated by extraction with chloroform. The obtained purified oily base was analyzed. For $C_{27}H_{33}N_3O_2S$ (463·4) calculated: 9·06% N, 6·91% S; found: 8·68% N, 6·96% S.

11-(1-(2-(4-(3-Hydroxypropyl)-1-piperazinyl)acetyl)-4-piperidylidene)-6,11-dihydrodibenzo[*b*,*e*]thiepin (*XII*)

A similar reaction of 2·40 g *IX* with 2·06 g 3-(1-piperazinyl)propanol[4] in 40 ml refluxing chloroform gave 3·1 g (99%) of crude oily *XII* which was transformed to the bis(hydrogen maleate), m.p. 110—113°C (ethanol). For $C_{36}H_{43}N_3O_{10}S$ (709·8) calculated: 60·92% C, 6·11% H, 5·92% N, 4·52% S; found: 61·00% C, 6·16% H, 5·84% N, 4·63% S.

The purified oily base *XII*, released from the salt similarly as in the preceding cases, was analyzed. For $C_{28}H_{35}N_3O_2S$ (477·7) calculated: 6·71% S; found: 6·68% S.

N-(2-(3,4-Dimethoxyphenyl)ethyl)-2-(4-methyl-1-piperazinyl)acetamide (*XIX*)

A similar reaction of 3·70 g of N-(2-(3,4-dimethoxyphenyl)ethyl)-2-chloroacetamide[13,14] with 3·16 g 1-methylpiperazine in 40 ml refluxing chloroform (1 h) gave 2·76 g (60%) of *XIX*, m.p. 82·5—83·5°C (benzene). Mass spectrum: 321 (M^+, $C_{17}H_{27}N_3O_3$, 4), 279 (4), 265 (4), 264 (4), 251 (2), 194 (3), 164 (13), 138 (1), 113 (100), 98 (11), 71 (10), 70 (67), 54 (8), 43 (10), 42 (16). IR spectrum: 813, 832, 850 (2 adjacent and solitary Ar–H); 1 029, 1 231, 1 263 ($ArOCH_3$); 1 587, 1 604, 3 010, 3 050 (Ar); 1 510, 1 660 (CONH); 2 670, 2 690, 2 735 (CH_3–N, CH_3–O); 3 380 (NH). ^{1}H NMR spectrum (100 MHz): 2·26 s, 3 H (NCH_3); 2·35 bm, 4 H ($CH_2N^4CH_2$ of piperazine); 2·42 bm, 4 H ($CH_2N^1CH_2$ of piperazine); 2·80 t, 2 H ($ArCH_2$); 2·96 s, 2 H ($COCH_2N$); 3·56 bq, 2 H (CH_2NH); 3·87 s, 6 H (2 OCH_3); 6·80 m, 3 H (ArH); 7·18 bt, 1 H (CONH). For $C_{17}H_{27}N_3O_3$ (321·4) calculated: 63·53% C, 8·47% H, 13·07% N; found: 63·63% C, 8·66% H, 12·83% N.

Bis(hydrogen maleate), m.p. 117—120°C (ethanol). For $C_{25}H_{35}N_3O_{11}$ (553·6) calculated: 54·24% C, 6·37% H, 7·59% N; found: 54·05% C, 6·46% H, 7·38% N.

2-Fluoro-6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ol (*XXIV*)

Ketone *XV* (ref.[15]) (1·0 g) was dissolved in 20 ml warm ethanol and the stirred solution was treated with a solution of 0·08 g $NaBH_4$ in 10 ml ethanol. The mixture was refluxed for 1 h, evaporated in vacuo, the residue was diluted with 10 ml water and extracted with chloroform. Processing of the extract gave 1·0 g (99%) of *XXIV*, m.p. 141—142·5°C (ethanol). IR spectrum: 728, 803, 889 (4 and 2 adjacent and solitary Ar–H); 1 039 (CHOH); 1 485, 1 588, 1 594, 3 020, 3 055, 3 095 (Ar); 3 530 (OH). ^{1}H NMR spectrum (100 MHz): 2·68 d, 1 H (OH, J = 3·0); 4·12 and 4·46 ABq, 1 + 1 H ($ArCH_2S$, J = 13·0); 6·28 d, 1 H (Ar_2CH–O, J = 3·0); 6·83 dt, 1 H (H-3); 7·00—7·60 m, 6 H (remaining ArH). For $C_{14}H_{11}FOS$ (246·3) calculated: 68·27% C, 4·50% H, 7·71% F, 13·02% S; found: 68·18% C, 4·51% H, 7·98% F, 13·00% S.

11-Chloro-2-fluoro-6,11-dihydrodibenzo[*b*,*e*]thiepin (*XXV*)

A solution of 1·0 g *XXIV* in 10 ml benzene was saturated for 30 min with HCl in the presence of 1·0 g $CaCl_2$. After standing overnight, the mixture was diluted with 10 ml benzene, $CaCl_2$ was filtered off, the filtrate was evaporated, and the residue was crystallized from a mixture of benzene and hexane; 0·90 g (84%) of *XXV*, m.p. 96—98°C. For $C_{14}H_{10}ClFS$ (264·7) calculated: 63·52% C, 3·81% H, 13·39% Cl, 7·18% F, 12·11% S; found: 63·62% C, 3·88% H, 13·32% Cl, 7·42% F, 11·95% S.

Ethyl 2-(4-Fluorophenylthiomethyl)benzoate (*XXVI*)

A solution of 0·50 g *XXII* (ref.[15]) in 17 ml ethanol was treated with 3·2 ml of a 8% solution of HCl in ethanol, the mixture was refluxed for 7 h, evaporated, the residue was diluted with

10 ml water and extracted with ether. Processing of the extract gave 0·50 g (90%) of *XXVI*, b.p. 140–152°C/0·40–0·55 kPa. UV spectrum: infl. 230 (4·11), infl. 275 (3·42). IR spectrum (film): 711, 765, 829 (4 and 2 adjacent Ar–H); 1 260 (C–O); 1 488, 1 589, 3 060 (Ar); 1 710 (ArCOOR). ^{1}H NMR spectrum (100 MHz): 1·37 t, 3 H (CH_3); 4·35 q, 2 H (OCH_2, J = 7·0); 4·44 s, 2 H ($ArCH_2S$); 6·80–7·40 m, 7 H (4 ArH of fluorophenyl and H-3, H-4, H-5 of benzoate); 7·95 m, 1 H (H-6 of benzoate). For $C_{16}H_{15}FO_2S$ (290·4) calculated: 66·19% C, 5·21% H, 6·54% F, 11·04% S; found: 66·06% C, 5·11% H, 6·28% F, 11·01% S.

A suspension of 0·45 g NaH in 15 ml dimethylformamide was treated with 0·21 g 2-propanol and the mixture was stirred for 30 min at 65–70°C. After cooling to 40°C, a solution of 1·00 g of *XXVI* in 10 ml dimethylformamide was added dropwise and the mixture was stirred for 5 h at 70°C. After cooling it was diluted with 40 ml water and extracted with chloroform. Processing of the extract gave 1·1 g oil which was chromatographed on 15 g silica gel. Chloroform eluted 0·60 g of crystals melting at 110–116°C which were recrystallized from a mixture of benzene and hexane, m.p. 113–116°C. IR spectrum: 771, 821 (4 and 2 adjacent Ar–H); 916, 1 272, 1 678, 2 520, 2 648, infl. 3 160 (ArCOOH); 1 487, 1 573, 1 589 (Ar). The analysis indicates that we are dealing with *XXII*. For $C_{14}H_{11}FO_2S$ (262·3) calculated: 64·11% C, 4·23% H, 7·24% F, 12·22% S; found: 64·00% C, 4·35% H, 7·33% F, 12·31% S. Ref.[15], m.p. 131–132°C.

2-Fluoroanthraquinone (*XXVII*)

Ketone *XV* (ref.[15]) (5·0 g) was dissolved in 30 ml dimethylformamide and the solution was slowly added to a stirred suspension of 2·70 g NaH in 40 ml dimethylformamide at room temperature. The dark violet mixture was stirred for 1·5 h at 50°C, poured into 300 ml water, and extracted with chloroform. Processing of the extract gave 4·85 g oily mixture which was chromatographed on 60 g silica gel. Elution with benzene gave first 0·5 g of yellowish needles melting at 118 to 120·5°C which proved to be pure monoclinic sulfur. Continued elution afforded 2·61 g (56%) of *XXVII*, m.p. 199–202°C (benzene). Mass spectrum: 226 (M^+, $C_{14}H_7FO_2$, 100), 225 (22), 198 (92), 170 (89), 150 (10), 85 (57). UV spectrum: 250 (4·64), 270 (3·79), 318 (3·82). IR spectrum: 710, 719, 853, 890 (4 and 2 adjacent and solitary Ar–H); 1 290 (C–O); 1 483, 1 572, 1 590, 3 070, 3 090 (Ar); 1 676 (CO of a 1,4-quinone). ^{1}H NMR spectrum (100 MHz): 7·48 m, 1 H (H-3); 7·85 m, 3 H (H-1, H-6, H-7); 8·35 m, 3 H (H-4, H-5, H-8). Ref.[22], m.p. 203–204°C.

2-Fluoro-9-methoxy-10-(methylthio)anthracene (*XXXI*)

A stirred suspension of 2·7 g NaH in 30 ml dimethylformamide was treated dropwise with a solution of 5·0 g *XV* (ref.[15]) in 35 ml dimethylformamide. The temperature of the mixture rose spontaneously to 45–50°C. After the exothermic reaction was over, 3·4 ml methyl iodide were added dropwise and the mixture was stirred for further 10 min. The mixture was decomposed by pouring into 75 ml water and was extracted with benzene. Processing of the extract gave 6·08 g of a dark, inhomogeneous residue which was flash chromatographed on 80 g silica gel Elution with a mixture 4 : 1 of light petroleum and benzene afforded first 1·46 g (26%) of yellow needles, melting at 121·5–122·5°C, identified as *XXXI*. Mass spectrum: 272 (M^+, $C_{16}H_{13}FOS$, 47), 257 (100), 242 (32), 214 (16), 170 (18), 140 (8), 136 (10), 81 (25), 69 (38). UV spectrum: 256 (5·05), 342 (3·47), 359 (3·75), 379 (3·92), 400 (3·91). IR spectrum: 770, 820, 870 (4 and 2 adjacent and solitary Ar–H); 1 081, 1 339, 1 357 ($ArOCH_3$); 1 480, 1 520, 1 550, 1 560, 3 020, 3 045, 3 065, 3 075(Ar). ^{1}H NMR spectrum (100 MHz): 2·38 s, 3 H (SCH_3); 4·12 s, 3 H (OCH_3); 7·20–7·60 m, 3 H (H-3, H-6, H-7); 7·90 dd, 1 H (H-1, J(H, H) = 2·0, J(H, F) = 9·0); 8·30 m, 1 H (H-8); 9·00 m, 2 H (H-4, H-5). ^{13}C NMR spectrum (50·3 MHz): 20·2 (SCH_3); 63·0 (OCH_3); 104·9 d (C-3, J(^{13}C, ^{19}F) = 22·2); 118·3 d (C-1, J(^{13}C, ^{19}F) = 27·4); 122·4, 125·7, 126·6, 127·3 (C-5, C-6, C-7, C-8); 125·2 d (C-9a, J(^{13}C, ^{19}F) = 8·8); 125·4 (C-8a); 127·1 (C-10); 130·5 d

(C-4, $J(^{13}C, ^{19}F) = 8{\cdot}6$); 132·2 (C-10a); 134·2 d (C-4a, $J(^{13}C, ^{19}F) = 1{\cdot}9$); 153·0 d (C-9, $J(^{13}C, ^{19}F) = 7{\cdot}6$); 160·3 d (C-2, $J(^{13}C, ^{19}F) = 248{\cdot}4$). For $C_{16}H_{13}FOS$ (272·3) calculated: 70·57% C, 4·81% H, 6·98% F, 11·77% S; found: 70·55% C, 4·80% H, 7·18% F, 11·98% S.

Further to be eluted was *XXVII* (0·35 g, 8%), m.p. 198·5—199·5°C, which was found identical (TLC) with the product of the preceding experiment.

The last to be eluted was 2,9-dimethoxy-10-(methylthio)anthracene (*XXXII*) in the yield of 1·33 g (24%), m.p. 118·5—120·5°C (benzene). Mass spectrum: 284 (M^+, $C_{17}H_{16}O_2S$), 269, 254. UV spectrum: 261 (5·30), 323 (3·21), 339 (3·52), 358 (3·72), 384 (3·81), 406 (3·84). IR spectrum: 768, 819, 828, 860 (4 and 2 adjacent and solitary Ar–H); 1 223 ($ArOCH_3$); 1 473, 1 552, 1 595 (Ar). ^{1}H NMR spectrum (100 MHz): 2·34 s, 3 H (SCH_3); 4·01 s and 4·10 s, 3 + 3 H (2 OCH_3); 7·30 dd, 1 H (H-3, J = 10·0; 2·5); 7·55 m, 3 H (H-1, H-6, H-7); 8·30 m, 1 H (H-8); 8·9 d, 1 H (H-4, J = 10·0); 8·92 m, 1 H (H-5). ^{13}C NMR spectrum (25·14 MHz): 20·32 q (SCH_3); 55·42 q (2-OCH_3); 62·52 q (9-OCH_3); 98·45 d (C-1); 121·75 d (C-3); 122·95 d (C-8); 125·49 d and 125·86 d (C-6, C-7); 127·36 d (C-5); 125·57 s, 126·09 s, 126·96 s, 132·4 s (C-4a, C-8a, C-9a, C-10a); 129·30 d (C-4); 133·44 s (C-10); 152·25 s and 157·42 s (C-2, C-9). For $C_{17}H_{16}O_2S$ (284·3) calculated: 71·82% C, 5·67% H, 11·26% S; found: 71·96% C, 5·61% H, 11·12% S.

9-Methoxy-10-(methylthio)anthracene (*XXXIII*)

A) A suspension of 5·91 g NaH in 70 ml dimethylformamide was stirred under nitrogen and treated dropwise with a solution of 10·0 g *XIV* (ref.[6]) in 55 ml dimethylformamide over 10 min. The temperature rose spontaneously to 38—40°C. It was stirred for 10 min, cooled to 20°C, and treated dropwise with a solution of 18·7 g methyl iodide in 25 ml dimethylformamide. The stirring was continued for 30 min without heating, then for 3 h at 40—45°C. After cooling, the mixture was decomposed by the addition of 150 ml water and extracted with benzene. Processing of the extract gave an oily residue which was dissolved in benzene and the solution was allowed to crystallize; 1·45 g of yellow substance melting at 150—154°C. The filtrate was evaporated and the residue (7·52 g) was chromatographed on 90 g silica gel. Elution with benzene gave 0·36 g product melting at 153—156°C, which was found identical with the compound obtained by crystallization (TLC). The total yield on this product, identified as *XXXIII*, was thus 1·81 g (16%), m.p. 153—156°C (benzene). Mass spectrum: 254 (M^+, $C_{16}H_{14}OS$, 55), 239 (100), 224 (26), 196 (14), 152 (17), 127 (8), 98 (8), 69 (10). UV spectrum: 257 (5·10), infl. 346 (3·46), 360 (3·74), 380 (3·93), 400 (3·87). IR spectrum: 768 (4 adjacent Ar–H); 1 086, 1 338 ($ArOCH_3$); 1 513, 1 547, 1 612, 3 035, 3 070 (Ar). ^{1}H NMR spectrum (100 MHz): 2·40 s, 3 H (SCH_3); 4·18 s, 3 H (OCH_3); 7·50 m, 4 H (H-2, H-3, H-6, H-7); 8·40 m, 2 H (H-1, H-8); 9·04 m, 2 H (H-4, H-5). ^{13}C NMR spectrum (50·3 MHz, $CDCl_3$–CD_3SOCD_3): 20·1 (SCH_3); 63·3 (OCH_3); 122·8, 125·2, 126·7, 127·2 (C-1, C-2, C-3, C-4, C-5, C-6, C-7, C-8); 124·9 (C-8a, C-9a); 126·3 (C-10); 134·8 (C-4a, C-10a); 153·8 (C-9). For $C_{16}H_{14}OS$ (254·4) calculated: 75·56% C, 5·55% H, 12·60% S; found: 75·64% C, 5·64% H, 12·68% S.

Continued elution with benzene gave 2·82 g (29%) of a compound melting at 154—155·5°C (benzene) which was identified as 10-hydroxy-10-methylanthrone (*XXXIV*). Mass spectrum: 224 (M^+, $C_{15}H_{12}O_2$, 1), 209 (100), 153 (10), 152 (20), 105 (10), 77 (14), 76 (16). UV spectrum: 272 (4·21). IR spectrum: 763 (4 adjacent Ar–H); 1 583, 1 600, 3 065 (Ar); 1 649 (Ar_2CO); 3 425 (OH). ^{1}H NMR spectrum (100 MHz): 1·62 s, 3 H (CH_3); 3·16 bs, 1 H (OH); 7·30—7·70 m, 4 H (H-2, H-3, H-6, H-7); 7·90 dd, 2 H (H-4, H-5); 8·20 dd, 2 H (H-1, 8). Ref.[29], m.p. 154 to 155°C.

B) A suspension of 1·11 g NaH in 40 ml dimethylformamide was stirred under nitrogen for 10 min and then treated with a solution of 5·00 g *XIV* (ref.[6]) in 25 ml dimethylformamide, added

dropwise over 30 min. The mixture was stirred for 30 min without heating and then for 45 min at 40—45°C. After cooling to 20°C, a solution of 12·5 g methyl iodide in 15 ml dimethylformamide was added dropwise over 30 min. The mixture was stirred for 4 h at room temperature, allowed to stand overnight, stirred for 1 h at 40°C and treated with a solution of further 12·5 g methyl iodide in 10 ml dimethylformamide. After 1 h stirring at room temperature, the mixture was stirred for 45 min at 40°C, cooled, decomposed with 80 ml water, and extracted with chloroform. The extract was washed with water and processed. The dark residue (8·67 g) was chromatographed on 150 g silica gel. The first to be eluted with benzene was *XXXIII* in the yield of 2·83 g (50%), m.p. 151—154°C (identical wtih the product obtained under *A*). It was followed by 1·00 g (18%) of a colourless substance melting at 110·5—112·5°C (benzene) which was identified as 10-methyl-10-(methylthio)anthrone (*XXX*). Mass spectrum: 254 (M^+, $C_{16}H_{14}OS$, 4), 208 (22), 207 (100), 179 (8), 178 (20), 152 (5). UV spectrum: 267 (3·91), infl. 300 (3·41). IR spectrum: 763 (4 adjacent Ar–H); 1 600, 3 055 (Ar); 1 650 (Ar_2CO). ^{1}H NMR spectrum (100 MHz): 1·40 s, 3 H (C–CH_3); 2·00 s, 3 H (SCH_3); 7·15—7·80 m, 4 H (H-2, H-3, H-6, H-7); 8·10 bd, 2 H (H-4, H-5, J = 8·0); 8·36 bd, 2 H (H-1, H-8). ^{13}C NMR spectrum (25·14 MHz): 12·73 q(10-CH_3); 32·72 q (SCH_3); 49·22 s (C-10); 126·76 d (C-4, C-5); 127·43 d (C-2, C-7); 128·67 d (C-1, C-8); 131·31 s (C-8a, C-9a); 133·85 d (C-3, C-6); 147·15 s (C-4a, C-10a); 183·00 s (C-9). For $C_{16}H_{14}OS$ (254·4) calculated: 75·56% C, 5·55U H, 12·60% S; found: 75·62% C, 5·69% H, 12·62% S.

The last to be eluted was 9,10-anthraquinone (*XXVIII*) in the yield of 0·61 g (13%), m.p. 242·5—244°C (benzene). Mass spectrum: 208 (M^+, $C_{14}H_8O_2$, 100), 180 (62), 152 (42), 151 (24), 126 (4), 90 (8), 76 (45). For $C_{14}H_8O_2$ (208·2) calculated: 80·76% C, 3·87% H; found: 80·34% C, 3·97% H. Refs[30,31], m.p. 285—286°C.

9-Methoxy-10-(methylsulfonyl)anthracene (*XXXV*)

A) This ether *XXXIII* (0·50 g) was dissolved in a warm mixture of 15 ml acetic acid and 5 ml benzene, the solution was cooled to 20°C, treated with 0·22 g 30% H_2O_2, and allowed to stand for 4 days at room temperature, a second portion of 30% H_2O_2 (0·45 g) was added. and the mixture was allowed to stand for further 3·5 days. It was diluted with 10 ml water, neutralized under cooling with NH_4OH, and extracted with chloroform. Processing of the extract gave a residue which was crystallized from a mixture of benzene and ethanol; 0·38 g (68%) of *XXXV*, m.p. 212—215°C (benzene–ethanol). UV spectrum: 258·5 (5·09), infl. 364 (3·68), infl. 379 (3·77), 392 (3·83), infl. 410 (3·64). IR spectrum (KBr): 773 (4 adjacent Ar–H); 1 133, 1 297 (SO_2); 1 487, 1 520, 1 550, 1 613, 3 005, 3 040, 3 085, 3 140 (Ar). ^{1}H NMR spectrum (80 MHz): 3·38 s, 3 H (SO_2CH_3); 4·20 s, 3 H (OCH_3); 7·55 m, 4 H (H-2, H-3, H-6, H-7); 8·42 m, 2 H (H-1, H-8); 9·42 m, 2 H (H-4, H-5). For $C_{16}H_{14}O_3S$ (286·3) calculated: 67·11% C, 4·93% H, 11·20% S; found: 67·44% C, 4·99% H, 11·29% S.

B) A solution of 0·30 g *XXXIII* in 10 ml dichloromethane was stirred and treated with a solution of 0·51 g *m*-chloroperbenzoic acid in 10 ml dichloromethane and the mixture was allowed to stand for 20 min at room temperature. The solution was diluted with chloroform, washed with 5% $NaHCO_3$ and 10% Na_2CO_3, dried, and evaporated. The residue (0·31 g) was chromatographed on 10 g silica gel. Elution with chloroform afforded 0·24 g (71%) of yellow needles, m.p. 212—215°C (benzene–ethanol), identical with the product, obtained under *A*).

10-(Methylsulfonyl)anthrone (*XXXVI*)

A mixture of 1·00 g *XXXIII*, 30 ml acetic acid and 1·20 g 30% H_2O_2 was refluxed for 2 h. On cooling two different types of crystals were formed (orange fine needles and yellowish needles) which were separated mechanically. The first substance (0·26 g, 32%) was identified as 9,10-

-anthraquinone (*XXVIII*), m.p. 248—249·5°C (benzene–ethanol) (direct comparison (TLC and IR spectrum) with *XXVIII*, obtained as a by-product of preparation of *XXXIII* under *B*).

The second substance (0·61 g, 57%) was identified as *XXXVI*, m.p. 237—239°C (toluene–ethanol). Mass spectrum (CI): 273 $(M + H)^+$, 271 $(M-H)^-$; EI: 193 (100), 192 (65), 165 (18), 82 (8). IR spectrum (KBr): 683 (4 adjacent Ar–H); 1 120, 1 316 (SO_2); 1 586, 1 597 (Ar); 1 664 (Ar_2CO). ^{1}H NMR spectrum (80 MHz): 2·92 s, 3 H (SO_2CH_3); 6·20 s, 1 H (Ar_2CHSO_2); 7·80 m, 6 H (H-2, H-3, H-4, H-5, H-6, H-7); 8·20 m, 2 H (H-1, H-8). ^{13}C NMR spectrum (25·14 MHz, CD_3SOCD_3, 80°C): 37·42 q (CH_3); 66·79 d (C-10); 126·39 d, 129·30 d, 130·79 d, 132·14 d, à 2 C (C-1, C-2, C-3, C-4, C-5, C-6, C-7, C-8); 131·54 s, 2 C and 133·26 s, 2 C (C-4a, C-8a, C-9a, C-10a). For $C_{15}H_{12}O_3S$ (272·3) calculated: 66·16% C, 4·44% H, 11·77% S; found: 66·38% C, 4·62% H, 11·32% S.

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