REACTIONS OF 4,4'-DISUBSTITUTED DIPHENYL SULFIDES WITH CHLOROACETYL CHLORIDE AND ALUMINIUM CHLORIDE

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Reactions of 4,4'-dihalogenodiphenyl sulfides *IIIa—IIIc* with chloroacetyl chloride and aluminium chloride afforded the enol forms of 2,8-dihalogeno-11-(chloroacetyl)dibenzo[*b*,*f*]thiepin-10(11*H*)-ones *IVa—IVc*. A similar reaction of di(4-methylphenyl) sulfide (*IIId*) resulted in 9-(chloromethylene)-2,7-dimethylthioxanthene (*Vd*) as the main product. Substitution reactions of *IVa* with piperidine and 1-methylpiperazine gave compounds *VI* and *VII* with the unchanged chelate system of the starting substance. A stepwise methylation of (2-phenylthiophenyl)acetonitrile resulted in the monomethyl derivative *XVI* and the dimethyl derivative *XVII* which afforded by alkaline hydrolysis the acids *XVIII* and *XIX*. Attempts at their cyclization with polyphosphoric acid to the corresponding 11-methylated dibenzo[*b*,*f*]thiepin-10(11*H*)ones are described.

In our previous communication[1] we described the reaction of di(4-chlorophenyl) sulfide with chloroacetyl chloride and aluminium chloride in dichloromethane with the aim of achieving a new synthesis of 2,8-dichlorodibenzo[*b*,*f*]thiepin-10(11*H*)-one[2]. It was clear that the desired course of the reaction, which presumed a double attacking of the diaryl sulfide by both active sites of the chloroacetyl chloride molecule under the formation of a seven-membered ring, is rather unlikely. It was, therefore not extremely surprising when a different compound was isolated as the reaction product, to which on the basis of analysis and the UV and IR spectra the structure *I* has been ascribed. This structure shows that two molecules of chloroacetyl chloride participated in the reaction. The reaction, however, was not carried out by making use of an excess of chloroacetyl chloride which was used only in the equimolecular quantity; the yield was approximately 25% when calculated on the starting diaryl sulfide, and approximately 50% calculated on chloroacetyl chloride. Approximately two years after the appearing of our communication[1], Granoth and coworkers[3,4] described a similar reaction of the 4,4'-disubstituted diaryl ethers with chloroacetyl chloride and aluminium chloride and obtained 9-(chloromethylene)xanthenes as products, *i.e.* the compound *II* in the case of using di(4-chlorophenyl) ether. Only one molecule of chloroacetyl chloride participated in the formation of these products and the reaction proceeded under the formation of a six-membered ring. The author

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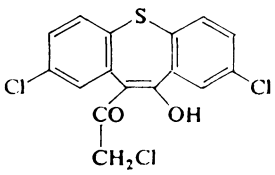
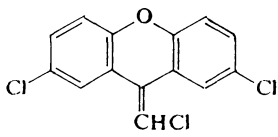
of the mentioned communications[5] expressed serious doubts about the correctness of the structure *I*, suggested by us, about the possibility of such important difference in the course of reactions of compounds which are structurally so similar (diaryl sulfides, diaryl ethers) and finally about the possibility of formation of a seven-membered ring in the Friedel–Crafts reaction when there does exist an evident possibility of the formation of a six-membered ring.



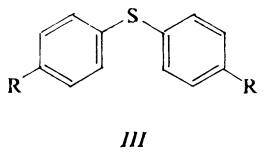
I



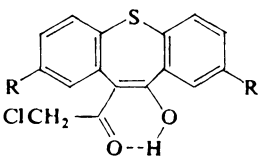
II

In this situation we considered necessary to reinvestigate the structure of the product of our reaction and to apply this reaction to some further structurally related compounds (preliminary communicatons ref.[6,7]). In the first part of the present communication we are presenting experimental details and some additional results. We repeated the experiment described previously[1]: by a reaction of equimolecular amounts of di(4-chlorophenyl) sulfide (*IIIa*) (ref.[8]) and chloroacetyl chloride with a small excess of aluminium chloride in dichloromethane first at room temperature and finally at the boiling point of the mixture we obtained in the yields stated a crystalline product with the melting point given previously. The mass spectrum prooved the composition $C_{16}H_9Cl_3O_2S$ which is in agreement with the analysis carried out previously and now once again. The fragmentation corresponds to the formula *I*: the base peak of *m/z* 321 corresponds to $C_{15}H_7Cl_2O_2S$ which is interpreted as the cation *A* (cleavage of CH_2Cl); a further abundant ion has the *m/z* 294 and corresponds to the radical cation of 2,8-dichlorodibenzo[*b*,*f*]thiepin-10(11*H*)-one (*B*). The ^{1}H NMR spectrum confirms likewise the formula *I* (we prefer now the formulation *IVa* with the six-membered chelate ring clearly shown): out of the aromatic protons only 1-H is differentiated and appears as a doublet at 8·03 ppm. The remaining aromatic protons are merged to a multiplet at about 7·50 ppm which corresponds to 6 protons and includes thus also the proton of the enol group =C—OH which is expressed by contracting of the multiplet to 5 protons after deuteration. The singlet at 4·80 ppm corresponds very well to the group $COCH_2Cl$. The formula *I* (or *IVa*) is thus fully corroborated and the thioxanthene structure *Va* cannot be considered for our compound at all. Carrying out of the experiment precisely under the conditions used for the diaryl ethers by the authors mentioned[4], gave the precisely same result as our experiment, *i.e.* the compound *IVa* in a yield of 50% (calculated per chloroacetyl chloride). An attempt at increasing the yield of compound *IVa*

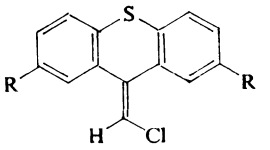
by using a twofold quantity of chloroacetyl chloride did not lead to the wanted result; the yield of compound *IVa*, on the contrary, was lower. 2,8-Dichlorodibenzo-[*b*,*f*]-thiepin-10(11*H*)-one[2] probably does not appear as a intermediate of the reaction because an attempt at preparing the 8-dechloro analogue of compound *IVa* by a reaction of 2-chlorodibenzo[*b*,*f*]thiepin-10(11*H*)-one (*VIII*) (ref.[2]) with chloroacetyl chloride and aluminium chloride in dichloromethane under analogous conditions did not lead to any reaction (the starting ketone *VIII* was recovered quantitatively).*



III

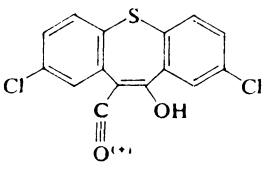


IV

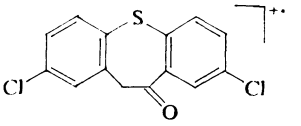


V

In formulae *III*–*V*: *a*, R = Cl; *b*, R = F; *c*, R = Br; *d*, R = CH_3



A



B

For checking a similar reaction with further diaryl sulfide substrates we prepared di(4-fluorophenyl) sulfide (*IIIb*) (ref.[9–12]), di(4-bromophenyl) sulfide (*IIIc*) (ref.[13–17]) and di(4-methylphenyl) sulfide (*IIId*) (ref.[18]) by reactions of the 4-substituted benzenediazonium hydrogen sulfate solutions with the 4-substituted sodium thiophenolates in the presence of copper (method, *cf.*[19,20]).

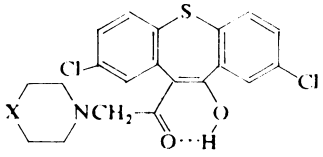
The reaction of *IIIb* with chloroacetyl chloride and aluminium chloride in dichloromethane under similar conditions which were used for *IIIa* gave as the single crystalline product *IVb* in a yield of 27%; the structure was determined by analysis and spectra (UV, IR and ^{1}H NMR). The reaction took thus the same course like in the case of the dichloro compound *IIIa*. An similar reaction of *IIIc* led to an oily mixture which was separated by chromatography on alumina in three inhomogeneous fractions. The only crystalline product was obtained from the middle fraction in a rather

* Added in the proof: The same result has recently been obtained with 2,8-dichlorodibenzo-[*b*,*f*]thiepin-10(11*H*)one[2]: no reaction with chloroacetyl chloride and aluminium chloride under the same conditions.

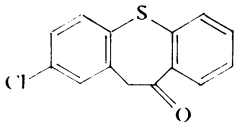
low yield and was characterized by analysis and IR spectrum as an analogue of the preceding products, *i.e. IVc*. A different course was taken by a similar reaction of *IIId*. From the crude product the analogue of the preceding compounds *IVd* was isolated by crystallization in a yield of only 4%; its elemental composition C_{18}. .$H_{15}ClO_2S$ was confirmed by the mass spectrum (*m/z* 330), as well as by analysis. The structure of the enolized diketone was corroborated by the UV, IR and ^{1}H NMR spectrum. The chromatography of the mother liquor on alumina afforded the main product of the reaction (yield of 48%) which is a crystalline substance $C_{16}H_{13}ClS$ (*m/z* 272). Its spectra (UV and ^{1}H NMR) are very similar to those of Granoth's products[3,4] and the structure of 9-(chloromethylene)-2,7-dimethylthioxanthene (*Vd*) could be ascribed to it without any doubts. Only in this case we were thus able to prepare a product of a similar type which is common in the diaryl ether–xanthene series.

Unsuccessful were our attempts at proving the structure of compound *IVa* (and in this way also of *IVb–IVd*) by chemical means, *i.e.* trials to transform compound *IVa* to some known dibenzo[*b*,*f*]thiepin derivative and achieve a direct correlation. The only reaction of compound *IVa* which afforded good yields on well characterized products were the substitution reactions with piperidine and 1-methylpiperazine in boiling chloroform. Amines were obtained to which according to analyses and spectra structures *VI* and *VII* were ascribed; their neutralization with acids gave crystalline salts. This reaction confirms only the presence of one reactive chlorine atom in the molecule of the starting compound but it does not contribute in any way to the proof of presence of the dibenzo[*b*,*f*]thiepin skeleton. Attempts at hydrolysis or ethanolysis of compound *IVa* by a solution of potassium hydroxide in aqueous ethanol, by sodium ethoxide in ethanol or in a mixture of ethanol and dimethylformamide, an attempt to reduce compound *IVa* with lithium aluminium hydride in tetrahydrofuran, as well as attempts to hydrolyze compound *VI* with a mixture of acetic and hydrochloric acid or at its reduction with sodium borohydride in aqueous methanol afforded oily mixtures from which only in some cases we were able to isolate minor crystalline products which, however, resisted to our attempts at their identification.

The only exception was the reaction of compound *IVa* with a boiling solution of potassium hydroxide in aqueous ethanol which afforded about 10% of a crystalline product with the elemental composition $C_{12}H_{11}ClO_3S$ (analysis and the mass



VI, X = CH_2
VII, X = NCH_3



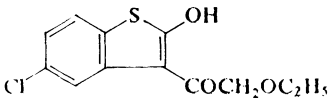
VIII

spectrum). According to the ^{1}H NMR spectrum, the reactive chlorine atom of the chloroacetyl residue was substituted with ethoxyl and the molecule shows the presence of a fragment —$COCH_2OCH_2CH_3$; the spectrum indicates further the presence of an acid hydrogen atom which is ascribed to the enolic hydroxyl C=C—OH (the presence of the hydroxyl group is confirmed also by the IR spectrum). The UV spectrum indicates a high degree of conjugation, even higher than that which is present in the starting compound *IVa*. The ^{1}H NMR spectrum identified further three well differentiated aromatic protons. This fact together with the elemental composition indicate that during the ethanolysis a cleavage of one chlorobenzene residue took place; all the data available led to formulating the product of ethanolysis and degradation by the tentative formula *IX*.

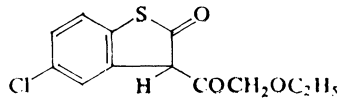
All this is very surprising because the transformation of *IVa* to *IX* would include *1*) cleavage of the S—Ar bond, *2*) cleavage of the CO—Ar bond and *3*) recyclization of the fragment formed by forming a new bond between the aliphatic chain and the sulfur atom. The cleavage of type *1*) and *2*) are known but they proceed only under extremely severe conditions: a cleavage of diphenyl sulfide to thiophenol and phenol was noted[21] on heating with an aqueous solution of sodium hydroxide and sodium sulfide in an autoclave to 350–360°C; thioxanthone is cleaved to 2-(phenylthio)-benzoic acid by fusion with potassium hydroxide at 230°C (ref.[22]). Our conditions were much milder which makes the possibility of transformation of compound *IVa* to substance *IX* rather unlikely [the ketone *VIII* (ref.[2]) when treated with a boiling solution of potassium hydroxide in aqueous ethanol under the conditions of our reaction remains unchanged].

As a contribution to elucidating this discrepancy we attempted at preparing compound *IX* by a simple and unequivocal synthesis. This was made easier by the fact that 5-chloro-3*H*-benzo[*b*]thiophen-2-one[23] was at our disposal. An attempt at processing this compound by treatment with ethyl ethoxyacetate[24] in the presence of sodium ethoxide in a boiling mixture of benzene and ethanol, *i.e.* under the conditions of the Claisen reaction, was unsuccessful (the starting material was recovered), but its acylation with ethoxyacetic anhydride[25] in the presence of sodium ethoxy acetate[24] at 100–110°C (method, *cf.*[26]) gave in a low yield a crystalline substance $C_{12}H_{11}ClO_3S$ (analysis and mass spectrum). It thus has the same composition like the product of ethanolysis of compound *IVa* from which it differs by the melting point and spectra. According to the ^{1}H NMR spectrum it is a 1 : 1 mixture of compound *IX* and its keto tautomer *X*; this is indicated by the fact that deuteration exchanges only one half of a hydrogen atom and further by the splitting of some signals. Because this compound was obtained by a rather unequivocal synthesis, we have to assume for it the structure *IX* + *X*. The result is that for the product, obtained by ethanolysis of compound *IVa*, the structure *IX* cannot be considered and it is only possible to consider the isomeric structure *XI*. This structure, however,

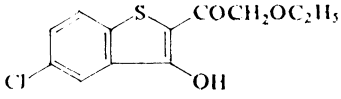
cannot be derived at all from the structure *IVa* which led us to doubts about the correctness of the structure *IVa*.



IX

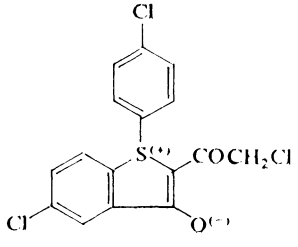


X

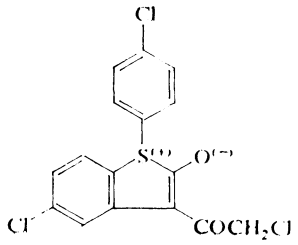


XI

The reaction of the sulfide *IIIa* with chloroacetyl chloride and aluminium chloride represents a number of possibilities and the products of these alternatives would contain in their molecules a chlorobenzene residue which could be much easier cleaved than in the case of structure *IVa* with the very stable dibenzo[*b*,*f*]thiepin skeleton. The cations formed primarily from chloroacetyl chloride can attack not only the *ortho*-positions of the benzene nuclei in the molecule of the sulfide *IIIa*,but also the sulfur atom. The products would then be on the one hand the dipoles (zwitterions) *XII* and *XIII*, and the ethers *XIV* and *XV* on the other, formed by the migration of the *p*-chlorophenyl cations; compounds *XII* and *XIV* appear more likely and they correspond to formula *XI* ascribed now to the product of ethanolysis. Compounds *XII* and *XIV* are isomeric with compound *I* (or *IVa*) and their spectra would be partly difficult to differentiate. There is, however, one fundamental difference: The molecule of compound *I* contains one prooven active hydrogen of the enolic hydroxyl group which enables the formation of a stable six-membered chelate, expressed by the formula *IVa*. The structure *IVa* remains thus even after this speculation valid and the only explanation of the formation of compound *XI* consists in the assumption that this compound is not formed at all from compound *IVa* but

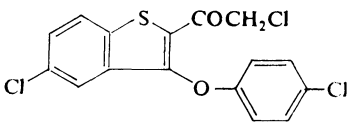


XII

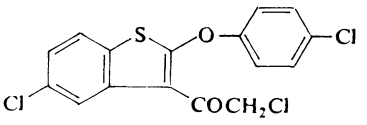


XIII

from a by-product of type *XII* or *XIV* contaminating the substance which was used in the solvolytic reactions.



XIV

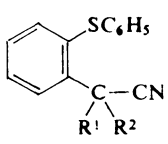


XV

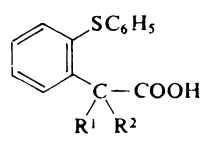
In the second part of this communication we are describing experiments aiming at the synthesis of 11-monomethyl and 11,11-dimethyl derivatives of dibenzo[*b*,*f*]-thiepin-10(11*H*)-one; while the monomethyl derivative *XXI* (ref.[27]) is known, the dimethyl derivative has not been described so far. Compound *XXI* was obtained by methylation of dibenzo[*b*,*f*]thiepin-10(11*H*)-one with methyl iodide after the preceding treatment with sodium amide[27]. When proceeding in this way, we could find a rather long time ago[28] that this method is not suitable for the purpose of preparation. The reaction of dibenzo[*b*,*f*]thiepin-10(11*H*)-one with sodium amide results evidently mainly in the enolate anion and the carbanion wanted is only a by-product; the following treatment with methyl iodide affords then a mixture of the C-methylated ketone *XXI* with a predominating amount of the enol methyl ether. Acidification of the mixture leads to the cleavage of the enol ether and to recovery of the starting ketone; the product is then a mixture of the starting ketone and the 11-methyl derivative *XXI* (*cf.*[29]) which is difficult to separate. For avoiding these difficulties we intended to use the analogy of a procedure which was used by our group for the preparation of dibenzo[*b*,*f*]thiepin-10(11*H*)-one derivatives alkylated in position 11 with butyl, benzyl or dimethylaminoalkyl[30]. This procedure consisted in the alkylation in the stage of a synthetic precursor, *i.e.* (2-phenylthiophenyl)acetonitrile[31]; the obtained α-alkylated nitriles were transformed by alkaline hydrolysis to the amides which were cyclized to the desired ketones with polyphosphoric acid.

A reaction of (2-phenylthiophenyl)acetonitrile[31] with sodium amide in benzene, the following treatment with a slight excess of methyl iodide in boiling benzene and the usual processing of the reaction mixture gave 76% of an oily rather sharply boiling product, which was found to be the almost homogeneous α-methyl nitrile *XVI*. The gas chromatography prooved the contamination with small quantities of the starting nitrile and the doubly methylated product. In agreement with that, its analysis is not completely correct; characterization with spectra (IR, ^{1}H NMR) confirms the structure *XVI*. Even the use of a 200% excess of sodium amide and methyl iodide does not enable a double methylation of (2-phenylthiophenyl)acetonitrile in a single step; the monomethyl derivative *XVI* is still the main product. For obtaining a homogeneous dimethyl derivative *XVII* it was necessary to repeat the methy-

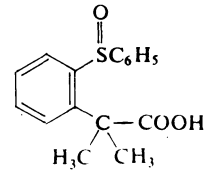
lation twice more. The identity of the product was established by the mass spectrum (*m/z* 253, $C_{16}H_{15}NS$, in agrement with the analysis) and further by the IR and ^{1}H-NMR spectra. The nitrile *XVI* was hydrolyzed without difficulties with a boiling solution of potassium hydroxide in aqueous ethanol affording the 2-(2-phenylthiophenyl)propionic acid (*XVIII*). For hydrolyzing the sterically hindered nitrile*XVII* it was necessary to use a longer refluxing with a solution of potassium hydroxide in ethylene glycol; the homogeneous acid *XIX* resulted in a yield of 75%.Hydrolysis using milder conditions gives in addition to a small amount of the acid *XIX* a large quantity of a neutral oily substance which is not the starting nitrile and which was considered the corresponding crude amide. For this reason, an attempt at its decomposition with nitrous acid in a mixture of sulfuric and acetic acid was carried out, first at room temperature and finally at 100°C (method[32]). A crystalline acid different from the acid *XIX* was obtained, containing in the molecule one atom of oxygen more; with the help of the IR spectrum and the course of the polarographic reduction it was characterized as the sulfoxide *XX*.



XVI, $R^1 = H$, $R^2 = CH_3$
XVII, $R^1 = R^2 = CH_3$



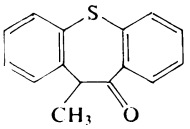
XVIII, $R^1 = H$, $R^2 = CH_3$
XIX, $R^1 = R^2 = CH_3$



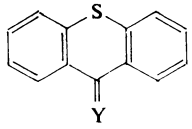
XX
$R^1 = R^2 = CH_3$

In the effort to prepare the 11-methylated derivatives of dibenzo[*b*,*f*]thiepin-10(11*H*)-one attempts at cyclization of the acids *XVIII* and *XIX* with polyphosphoric acid (method[33]) were carried out. A reaction of the acid *XVIII* with a tenfold quantity of polyphosphoric acid at 115–120°C for 3 h resulted in a high yield of a neutral inhomogeneous product which was separated by chromatography on aluminium oxide. The main product was eluted with benzene as an almost homogeneous oily substance as the least polar component of the mixture. It was purified by distillation and identified by analysis and spectra, especially by means of the mass spectrum, as the desired 11-methyldibenzo[*b*,*f*]thiepin-10(11*H*)-one (*XXI*); the yield on the pure substance was about 50%. In disagreement with the literature[27] which describes this compound as a crystalline one, we were not able to induce its crystallization. From a somewhat more polar fraction from the chromatography a very small amount of a further crystalline substance was obtained, identified on the basis of analysis, spectra and comparison with an authentic substance as thioxanthone (*XXII*) (ref.[34,35]). In the second cyclization experiment with the acid *XVIII* there was used a substantially greater excess of polyphosphoric acid (24-fold amount by weight), a lower reaction temperature (60–80°C) and a longer reaction time (24 h). The

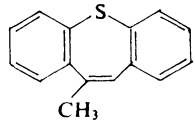
neutral inhomogeneous product was obtained in a substantially lower yield (about 50%) and from its solution in benzene a small amount of thioxanthone (*XXII*) crystallized. The oily residue after the evaporation of the mother liquor was again chromatographed on alumina. The main little polar fraction did not contain in this case the ketone *XXI*. After its rechromatography there was isolated in small quantity a further crystalline substance $C_{13}H_{10}S$ (mass spectrum and analysis), which was identified by means of the ^1H NMR spectrum and by comparison with the authentic product as thioxanthene (*XXIII*) (ref.[35,36]). Thioxanthone (*XXII*) and thioxanthene (*XXIII*) are the by-products of the cyclization reaction resulting by cleavage of the molecule of the starting substance *XVIII*. Their simultaneous appearing here in approximately equimolecular quantities indicates that the thioxanthylium cation is their common precursor, about which it is known that it disproportionates on hydrolysis to compounds *XXII* and *XXIII* (ref.[35,37]).



XXI



XXII, Y = O
XXIII, Y = H_2
XXV, Y = CH_2



XXIV

The acid *XIX* was used in a cyclization experiment in which a 24-fold quantity of polyphosphoric acid was used and the reaction was carried out for 30 h at 100°C. After decomposition of the mixture with water and extraction with benzene there was isolated only 35% of an inhomogeneous neutral product; the rest remained dissolved in the acid aqueous layer. According to chromatography of a sample of the neutral product on a thin-layer of silica gel it consists of at least three components. Chromatography on alumina separated first the least polar fraction whose rechromatography gave a small amount of a nonpolar crystalline compound $C_{15}H_{12}S$ (mass spectrum and analysis) to which on the basis of the ^1H NMR spectrum the structure of 10-methyldibenzo[*b*,*f*]thiepin (*XXIV*) was ascribed. The literature[27,38] described the preparation of this substance differently and gave a substantially lower melting point value. As a somewhat more polar compound, there was eluted again in a small amount a further crystalline compound which is according to the mass spectrum and analysis a lower homologue of the preceding substance, *i.e.* has the elemental composition $C_{14}H_{10}S$. With regard to the fact that we are not dealing here with dibenzo[*b*,*f*]thiepin (being well known to us[31]), we ascribe to it tentatively the structure of 9-methylenethioxanthene (*XXV*). This compound was mentioned in literature[39] and its properties were described as being heavily different from the properties of our substance. The main product of cyclization in this case is the most

polar component, resulting in a yield of about 20%; it is an oil which distills without decomposition and which was identified by analysis and spectra again as 11-methyldibenzo[*b,f*]thiepin-10(11*H*)-one (*XXI*). 11,11-Dimethyldibenzo[*b,f*]thiepin-10(11*H*)-one could not be prepared at all. The formation of the monomethyl ketone has to be explained by the cleavage of one methyl group from the little reactive, sterically hindered acylium ion, which only after this removal of the hindrance is able to cyclize. The formation of compound *XXV* can be explained by stabilization of the 9-methylthioxanthylium ion by cleavage of a proton. We have no explanation for the formation of compound *XXIV*.

Finally we would like to note that Japanese authors[40] used our approach in synthesizing tricyclic ketones with the seven-membered central ring with a quaternary carbon adjacent to the keto group starting from α,α-dialkylated arylacetonitriles; in this way they were able to construct dibenz[*b,f*]oxepin and dibenzo[*a,d*]cycloheptene skeletons. On the other hand a similar attempt at building the dibenzo[*b,f*]thiepin skeleton met with serious difficulties already in the step of α,α-dialkylation of the starting nitrile (the yield of only 8%).

EXPERIMENTAL

The melting points of analytical preparations were determined in the Mettler FP-5 melting point recorder. The samples were dried at about 60 Pa over P_2O_5 at room temperature or at 77°C. UV spectra (in methanol) were recorded with a Unicam SP 8000 spectrophotometer, the IR spectra (mostly in Nujol) with a Unicam SP 200G spectrophotometer, the ^1H NMR spectra (in C^2HCl_3 unless stated otherwise) with a Tesla BS 487C (80 MHz) spectrometer, the ^{19}F NMR spectra (in $CHCl_3$, $\delta_{CFCl_3} = 0$) with the same instrument and the mass spectra with the MS 902 (AEI), Varian MAT 311, Varian MAT 44S and MCH 1320 spectrometers. The homogeneity of the compounds and the composition of the mixtures were checked by thin-layer chromatography on silica gel (Silufol). Preparative chromatographic separations were carried out on columns of neutral aluminium oxide (activity *II*).

2,8-Dichloro-11-(chloroacetyl)dibenzo[*b,f*]thiepin-10-ol (*I, IVa*)

The reaction of 10·2 g 4,4'-dichlorodiphenyl sulfide[8], 4·5 g chloroacetyl chloride and 5·9 g $AlCl_3$ in 40 ml dichloromethane was carried out similarly like described in our previous paper[1]. After decomposition of the mixture with 100 ml 3M-HCl it was extracted with dichloromethane. The extract was washed with 5% NaOH and water, dried with K_2CO_3 and evaporated. The residue was treated with 30 ml warm benzene and the solution was allowed to crystallize; 3·85 g (52% calculated per chloroacetyl chloride), m.p. 215—217°C. Analytical sample, m.p. 217—218°C (needles from toluene). Mass spectrum, *m/z* (%): 370 (M^+ corresponding to $C_{16}H_9Cl_3O_2S$ by high resolution, 6%), 336 (9), 321 (100, $C_{15}H_7Cl_2O_2S$, *A*), 294 (70, $C_{14}H_8Cl_2OS$, *B*), 258 (76), 231 (13), 224 (10), 218 (15), 210(39), 195 (24), 186 (14), 168 (17), 154 (39), 119 (20), 111 (16), 75 (35). ^1H NMR spectrum: δ 8·03 (d, J = 2·0 Hz, 1 H, 1-H), *c.* 7·50 (m, 6 H, after ^2H_2O 5 H, remaining 5 ArH and =C—OH), 4·80 (s, 2 H, $COCH_2Cl$). Our previous[1] m.p. value was 216 to 217°C. Analysis and the UV and IR spectra were included in the previous communication[1]. Evaporation of the mother liquor recovered 4·20 g starting *IIIa*, m.p. 93—95°C (the yield of *IVa* per conversion is 44%).

Di(4-fluorophenyl) Sulfide (*IIIb*)

A solution of 31·6 g 4-fluoroaniline in 275 ml water and 18·8 ml H_2SO_4 was stirred and diazotized at 0—5°C with a solution of 21·5 g $NaNO_2$ in 40 ml water over 1 h. The solution formed was treated Cith 11 g sodium acetate trihydrate and the solution was added dropwise over 1 h to a stirred mixture of a solution of 36·4 g NaOH and 38·0 g 4-fluorothiophenol[41] in 170 ml water and of 2 g Cu which was heated to 60—70°C. The stirring and heating was continued for 45 min, the mixture was cooled, diluted with 300 ml water and the product was extracted with benzene. The extract was filtered, washed with 3M-HCl, 5% NaOH and water, dried with $CaCl_2$ and distilled; 36·1 g (57%), b.p. 136—138°C/1·33 kPa. Analytical sample, b.p. 130—132°C/1·07 kPa. Lit.[9,12], b.p. 136—137°C/1·2 kPa, and 133—135°C/0·93 kPa, respectively.

Di(4-bromophenyl) Sulfide (*IIIc*)

4-Bromoaniline (16·5 g) in 120 ml water and 6·3 ml H_2SO_4 was diazotized with 6·9 g $NaNO_2$ in 20 ml water and the solution was treated with 3·65 g sodium acetate trihydrate and processed by dropping into a solution of 18·8 g 4-bromothiophenol[42] and 12·3 g NaOH in 60 ml water to which 1 g Cu was added. The benzene extract of the crude product was evaporated. The solid residue was crystallized from 200 ml ethanol; 11·9 g (35%), m.p. 100—105°C. Analytical sample, m.p. 110—111°C (ethanol). Lit[13—17], m.p. values between 109 and 115°C.

11-(Chloroacetyl)-2,8-difluorodibenzo[*b*,*f*]thiepin-10-ol (*IVb*)

A mixture of 11·1 g *IIIb*, 8·6 g $AlCl_3$ and 100 ml dichloromethane was cooled with ice and treated under stirring with a solution of 6·2 g chloroacetyl chloride in 10 ml dichloromethane. The mixture was stirred and refluxed for 5 h, cooled and decomposed by a slow addition of 100 ml water. The organic layer was separated, washed with 100 ml 5% NaOH, dried with K_2CO_3 and evaporated. The solid residue was boiled for 1 min with 30 ml benzene, the mixture was allowed to stand overnight at room temperature and the product was filtered; 4·5 g (27%), m.p. 172—173°C. Analytical sample, m.p. 175°C (ethanol). UV spectrum: λ_{max} 340 nm (log ε 4·00), inflexes at 233 nm (4·32), 267 nm (3·80) and 300 nm (3·85). IR spectrum: 826, 832, 841, 849, 891 (2 adjacent and solitary Ar—H), 1 288 (C—O), 1 386 (C—F), 1 582, 1 600 (Ar and C=C of enol), 1 642 (=C—C=O···H—O—C= in a 6-membered chelate ring), 3 058, 3 080, 3 108 cm^{-1} (Ar). ^1H NMR spectrum: δ 7·00—7·90 (m, 7 H, 6 ArH and C=C—OH), 4·82 (s, 2 H, $COCH_2Cl$). ^{19}F NMR spectrum: δ −103·7 and −104·2 (2 m, 1 + 1 F). For $C_{16}H_9ClF_2O_2S$ (338·7) calculated: 56·73% C, 2·68% H, 10·46% Cl, 11·22% F, 9·46% S; found: 56·70% C, 2·61% H, 10·71% Cl, 11·46% F, 9·54% S.

2,8-Dibromo-11-(chloroacetyl)dibenzo[*b*,*f*]thiepin-10-ol (*IVc*)

A stirred mixture of 9·5 g *IIIc*, 4·8 g $AlCl_3$ and 80 ml dichloromethane was cooled with ice and treated over 10 min with a solution of 3·5 g chloroacetyl chloride in 10 ml dichloromethane. The mixture was refluxed for 2 h, cooled and decomposed with 100 ml water. The organic layer was washed with 5% NaOH, dried with K_2CO_3 and evaporated. The residue was diluted with 20 ml benzene and chromatographed on 200 g Al_2O_3. Benzene eluted 4·50 g starting *IIIc* (m.p. 110 to 111°C). Chloroform eluted then 1·75 g (26% per conversion) crude *IVc* which crystallized from benzene, m.p. 196—201°C (brownish prisms). IR spectrum (KBr): 762 (C—Cl), 820, 880 (2 adjacent and solitary Ar—H), 1 096, 1 135 (C—O in =C—OH), 1 382, 1 413 (C—H in CH_2CO), 1 570, 1 600 (Ar and C=C of enol), 1 633 (=C—C=O···H—O—C= in a 6-membered chelate ring), 3 080 cm^{-1} (Ar). For $C_{16}H_9Br_2ClO_2S$ (460·6) calculated: 41·72% C, 1·97% H; found: 41·55% C, 2·16% H.

9-(Chloromethylene)-2,7-dimethylthioxanthene (*Vd*)

A mixture of 10·72 g *IIId* (ref.[18]), 8·6 g $AlCl_3$ and 100 ml dichloromethane was cooled with ice and treated under stirring with a solution of 6·2 g chloroacetyl chloride in 10 ml dichloromethane. The mixture was refluxed for 5 h, cooled and decomposed with 100 ml water. After dilution with dichloromethane, the organic layer was separated, washed with 100 ml 5% NaOH, dried with K_2CO_3, filtered and evaporated. The residue was dissolved in a warm mixture of 15 ml ethanol and 30 ml light petroleum and the solution was allowed to crystallize; 0·6 g (4%) 11-(chloroacetyl)-2,8-dimethyldibenzo[*b*,*f*]thiepin-10-ol (*IVd*), m.p. 198–199°C (ethanol). Mass spectrum, *m*/*z* (%): 330 (M^+ corresponding to $C_{18}H_{15}ClO_2S$, 10%), 295 (6, M–15), 281 (95, M–CH_2Cl), 254 (73), 253 (100, M–$COCH_2Cl$), 238 (25), 225 (15). UV spectrum: λ_{max} 328 nm (log ε 4·01), inflexes at 235 nm (4·43), 270 nm (3·95). IR spectrum: 815, 903 (2 adjacent and solitary Ar—H), 1 588, 1 602 (Ar and C=C of enol), 1 632 cm^{-1} (=C—C=O···H—O—C= in a 6-membered chelate ring). ^1H NMR spectrum: δ 7·85 (s, 1 H, 1-H), 7·40 to 7·50 (m, 6 H, remaining ArH and =C—OH), 4·80 (s, 2 H, $COCH_2Cl$), 2·50 and 2·32 (2 s, 3 + 3 H, 2 $ArCH_3$). For $C_{18}H_{15}ClO_2S$ (330·8) calculated: 65·35% C, 4·57% H, 10·72% Cl, 9·69% S; found: 65·17% C, 4·68% H, 10·80% Cl, 9·55% S.

The mother liquor was evaporated, the residue was dissolved in benzene and chromatographed on 250 g Al_2O_3. Benzene eluted 6·6 g (48%) homogeneous oil which crystallized after treatment with 10 ml light petroleum; 4·05 g (30%) almost pure *Vb*, m.p. 113–114·5°C. Analytical sample, m.p. 115°C (ethanol). Mass spectrum, *m*/*z* (%): 272 (M^+ corresponding to $C_{16}H_{13}ClS$, 100%), 257 (4, M–15), 239 (22), 237 (18), 222 (20), 221 (20). UV spectrum: λ_{max} 271 nm (log ε 4·21), 335 nm (3·53). IR spectrum: 807, 819, 895, 905 (2 adjacent and solitary Ar—H), 842 (R_2C=CHR′), 1 592, 3 090 cm^{-1} (Ar). ^1H NMR spectrum: δ 6·90–7·70 (m, 6 H, ArH), 6·40 (s, 1 H, C=CHCl), 2·35 and 2·30 (2 s, 3 + 3 H, 2 $ArCH_3$). For $C_{16}H_{13}ClS$ (272·8) calculated: 70·45% C, 4·80% H, 13·00% Cl, 11·75% S; found: 70·34% C, 4·95% H, 13·00% Cl, 11·61% S.

2,8-Dichloro-11-(piperidinoacetyl)dibenzo[*b*,*f*]thiepin-10-ol (*VI*)

A mixture of 4·1 g *IVa*, 15 ml chloroform and 4·4 g piperidine was stirred and refluxed for 3 h. Chloroform was evaporated, the residue was diluted with 150 ml benzene, the solution was washed with water and then shaken with 65 ml 3M-HCl. The aqueous layer together with the oily hydrochloride was separated, treated with aqueous NH_3 and the base was extracted with benzene. The extract was dried with K_2CO_3 and evaporated under reduced pressure; 3·7 g (81%) oil which crystallized after treatment with acetone, m.p. 180–183°C. Analytical sample, m.p. 184–185°C (ethanol). Mass spectrum, *m*/*z* (%): 419 (M^+ corresponding to $C_{21}H_{19}Cl_2NO_2$.S, 2%), 336 (2), 321 (1), 309 (5), 308 (5), 278 (2), 98 (100, $C_5H_{10}N^+$=CH_2). UV spectrum: λ_{max} 226 nm (log ε 4·50), 271 nm (4·03), 325 nm (4·02), inflex at 244 nm (4·43). IR spectrum: 840, 849, 901 (2 adjacent and solitary Ar—H), 1 130 (C—O of =C—OH), 1 480, 1 576, 3 050, 3 060, 3 090 (Ar), 1 599, 1 626 cm^{-1} (=C—C=O···H—O—C= in a 6-membered chelate ring). ^1H NMR spectrum: δ 7·99 (d, 1 H, 1-H), 7·20–7·70 (m, 6 H, 5 ArH and =C—OH), 3·85 (s, 2 H, $COCH_2N$), 2·50 (m, 4 H, CH_2NCH_2 of piperidine), 1·50 (m, 6 H, remaining 3 CH_2 of piperidine). For $C_{21}H_{19}Cl_2NO_2S$ (420·4) calculated: 60·00% C, 4·55% H, 16·87% Cl, 3·33% N, 7·63% S; found: 59·84% C, 4·92% H, 16·68% Cl, 3·45% N, 7·63% S.

Hydrogen succinate, m.p. 159–160°C (ethanol). For $C_{25}H_{25}Cl_2NO_6S$ (538·5) calculated: 55·78% C, 4·68% H, 13·17% Cl, 2·60% N, 5·95% S; found: 55·86% C, 4·76% H, 13·22% Cl, 2·61% N, 6·08% S.

2,8-Dichloro-11-(4-methylpiperazinoacetyl)dibenzo[*b*,*f*]thiepin-10-ol (*VII*)

A mixture of 1·85 g *IVa*, 8 ml chloroform and 2·35 g 1-methylpiperazine was stirred and refluxed for 4 h. Similar processing like in the preceding case gave 1·40 g (65%) crude product which crystallized from ethanol, m.p. 196°C. UV spectrum: λ_{max} 272 nm (log ε 4·04), 326 nm (4·04), inflexes at 241 nm (4·44), 312 nm (4·03) and 340 nm (3·99). IR spectrum: 839, 835, 900, 912 (2 adjacent and solitary Ar—H), 1 332 (C—O in =C—OH), 1 580, 1 599, 1 633 (=C—C=O... ...H—O—C= in the 6-membered chelate ring), 2 800 cm^{-1} (N—CH_3). ^{1}H NMR spectrum: δ 7·98 (d, 1 H, 1-H), 7·20—7·60 (m, 6 H, 5 ArH and =C—OH), 3·90 (s, 2 H, $COCH_2N$), 2·30 to 2·90 (m, 8 H, 4 CH_2N of piperazine), 2·20 (s, 3 H, NCH_3). For $C_{21}H_{20}Cl_2N_2O_2S$ (435·4) calculated: 57·93% C, 4·63% H, 16·29% Cl, 6·43% N, 7·36% S; found: 58·20% C, 4·54% H, 16·15% Cl, 5·74% N, 7·47% S.

Bis(*hydrogen maleate*), m.p. 153—154°C (ethanol). For $C_{29}H_{28}Cl_2N_2O_{10}S$ (667·5) calculated: 52·18% C, 4·23% H, 10·62% Cl, 4·20% N, 4·80% S; found: 51·78% C, 4·38% H, 10·73% Cl, 4·25% N, 5·04% S.

5-Chloro-3-(ethoxyacetyl)benzo[*b*]thiophene-2-ol (*IX*, *X*)

A mixture of 2·5 g 5-chloro-3*H*-benzo[*b*]thiophen-2-one[23], 10·5 g ethoxyacetic anhydride[25] and 1·0 g sodium ethoxyacetate[24] was heated for 2 h to 100—110°C and poured into water. The precipitate was refluxed for 1 h with a 5% solution of $NaHCO_3$, filtered and the filtrate was acidified with hydrochloric acid; the precipitate was filtered and dried, 0·7 g (19%), m.p. 112—114°C and after a change of the crystal form (resolidification) a second m.p. 124—125°C (benzene–light petroleum). Mass spectrum, *m*/*z*: 270 (M^+ corresponding to $C_{12}H_{11}ClO_3S$). UV spectrum: λ_{max} 233 nm (log ε 4·36), 263 nm (4·06), 277·5 nm (4·08), 310 nm (4·06). IR spectrum: 807, 851, 885 (2 adjacent and solitary Ar—H), 1 125, 1 332, 1 352 (C—O in CO and =C—OH), 1 553 (Ar), 1 605, 1 678 (=C—C=O...H—O—C= in the 6-membered chelate ring), 3 150, 3 245 cm^{-1} (OH in H bond). ^{1}H NMR spectrum: δ 9·10 (bs, 0·5 H, =C—OH in *IX*), 7·85 and 7·40 (2 bs, 1 H, 4-H), *c*. 7·15 (bm, 2 H, 6,7-H_2), 4·70 (s, 0·5 H, ArCHCO in *X*), 4·48 (s, 2 H, $COCH_2O$), 3·80 (q, 2 H, CH_2O in ethoxyl), 1·30 (t, 3 H, CH_3 in ethoxyl). For $C_{12}H_{11}ClO_3S$ (270·7) calculated: 53·24% C, 4·10% H, 13·10% Cl, 11·84% S; found: 54·02% C, 4·17% H, 12·90% Cl, 11·40% S.

5-Chloro-2-(ethoxyacetyl)benzo[*b*]thiophene-3-ol (*XI*)

Crude *IVa* (1·5 g) was refluxed for 3 h with a solution of 2·0 g KOH in 15 ml ethanol. The mixture was diluted with 250 ml water, the solution formed was filtered, the filtrate was acidified with 3M-HCl and extracted with benzene. After drying (Na_2SO_4) the extract was evaporated, the residue was dissolved in 80% aqueous ethanol and the solution was allowed to stand for 2 weeks. The small quantity of crystals was separated, dissolved in 2 ml 1 : 1 mixture of ethanol and benzene, the undissolved part was filtered off and the filtrate was evaporated *in vacuo*. The crystalline residue was crystallized from 0·5 ml ethanol; 0·10 g (9%), m.p. 70—72°C. Mass spectrum, *m*/*z*: 270 (M^+ corresponding to $C_{12}H_{11}ClO_3S$). UV spectrum: λ_{max} 257·5 nm (log ε 4·15), 288 nm (4·12), 322·5 nm (4·11), 404 (3·85), infl. at 312 nm (4·06). IR spectrum (KBr): 810, 877 (2 adjacent and solitary Ar—H), 1 099 (R—O—R'), 1 193 (C—O in =C—OH), 1 269 (C—O in CO), 1 529, 1 569 (Ar), 1 617 and 1·652 (=C—C=O...H—O—C= in a 6-membered chelate ring), 3 430 cm^{-1} (OH). ^{1}H NMR spectrum: δ 12·30 (bs, 1 H, =C—OH), 7·90 (d, J = 2·5 Hz, 1 H, 4-H), 7·60 (*d*, J = 8·0 Hz, 1 H, 7-H), 7·40 (q, J = 8·0; 2·5 Hz, 1 H, 6-H), 4·28 (s, 2 H, $COCH_2O$), 3·68 (q. J = 7·0 Hz, 2 H, OCH_2 of ethoxyl), 1·35 (t, J = 7·0 Hz, 3 H, CH_3 in ethoxyl). For C_{12}·

$.H_{11}ClO_3S$ (270·7) calculated: 53·24% C, 4·10% H, 13·09% Cl, 11·84% S; found: 53·39% C, 4·18% H, 13·28% Cl, 11·81% S.

2-(2-Phenylthiophenyl)propionitrile (*XVI*)

A mixture of 48 g (2-phenylthiophenyl)acetonitrile[31], 500 ml benzene and 15 g 70% $NaNH_2$ was stirred and refluxed for 1·5 h. After cooling it was treated with 40 g methyl iodide and the refluxing was continued for 7 h. The cooled mixture was decomposed with water, washed with 1M-HCl and with water, dried with K_2CO_3 and distilled; 38·7 g (76%), b.p. 130—142°C/13 Pa. Redistillation gave 27·6 g fraction boiling at 136—140°C/13 Pa containing 95% *XVI* according to gas chromatography. A sample for analysis was redistilled, b.p. 138—140°C/13 Pa. IR spectrum (film): 690, 740, 750 (5 and 4 adjacent Ar—H), 1 471, 1 480, 1 583, 3 036 (Ar), 2 233 cm^{-1} (R—CN). ^1H NMR spectrum: δ 7·00—7·80 (m, 9 H, ArH), 4·55 (q, J = 7·0 Hz, 1 H, ArCHCN), 1·50 (d, J = 7·0 Hz, 3 H, CH_3). For $C_{15}H_{13}NS$ (239·3) calculated: 75·28% C, 5·47% H, 5·85% N; found: 74·43% C, 5·44% H, 5·65% N.

2-Methyl-2-(2-phenylthiophenyl)propionitrile (*XVII*)

A mixture of 33 g 70% $NaNH_2$, 700 ml benzene and 100 g (2-phenylthiophenyl)acetonitrile[31] was stirred and refluxed for 2 h. After cooling the mixture was treated dropwise over 30 min with 82 g methyl iodide (exothermic reaction). It was allowed to stand overnight and then refluxed for 7 h. After cooling it was decomposed by a slow addition of 500 ml water. The benzene layer was washed with water, dried with K_2CO_3 and evaporated. The residue (106 g) was dissolved in 300 ml benzene and the solution was added to a suspension of 33 g 70% $NaNH_2$ in 400 ml benzene. The mixture was refluxed and stirred for 7 h, allowed to stand at room temperature for 36 h, treated dropwise over 30 min with 80 g methyl iodide and when the exothermic reaction was over, it was refluxed for 7 h. After standing overnight the mixture was decomposed with water, the benzene layer was washed with water, dried and evaporated under reduced pressure. The residue (98 g) was distilled; 67 g, b.p. 158—174°C/67 Pa. Because it was prooven by gas chromatography that the product still contains *XVI*, the methylation was repeated once again. The distillate was dissolved in 450 ml benzene, the solution was treated with 13 g 70% $NaNH_2$ and the mixture was stirred and refluxed for 6 h. After cooling it was treated with 45 g methyl iodide, allowed to stand overnight at room temperature, stirred and refluxed for 7 h, cooled and decomposed with water. The benzene layer was washed with 150 ml 3M-HCl, 200 ml dilute aqueous NH_3 and water, it was dried and distilled; 50·6 g, b.p. 150—158°C/53 Pa. According to gas chromatography, even this product is not homogeneous. On standing for 3 weeks, crystallization took place; 21·5 g (19%) homogeneous *XVII*, m.p. 105—106°C (benzene–hexane). Mass spectrum. m/z: 253 (M^+ corresponding to $C_{16}H_{15}NS$). IR spectrum (KBr): 700, 763, 770 (5 and 4 adjacent Ar—H), 1 483, 1 586, 1 599, 3 056 (Ar), 2 040 cm^{-1} (R—CN); in Nujol: 699, 760, 1 492, 1 586, 1 598, 2 220 cm^{-1}. ^1H NMR spectrum: δ 7·20—7·70 (m, 9 H, ArH), 2·20 and 2·12 (2 s, 3 + 3 H, 2 C—CH_3). For $C_{16}H_{15}NS$ (253·4) calculated: 75·85% C, 5·97% H, 5·53% N, 12·65% S; found: 75·76% C, 6·17% H, 5·48% N, 12·53% S.

2-(2-Phenylthiophenyl)propionic Acid (*XVIII*)

A solution of 6·5 g *XVI* in 25 ml ethanol was treated with 15 ml 50% aqueous KOH and the mixture was stirred and refluxed for 7 h. Ethanol was evaporated, the residue was diluted with water and the solution washed with benzene. It was then acidified with 15 ml hydrochloric acid and the product was extracted with benzene. Processing of the extract gave a residue which

crystallized after treatment with a mixture of 10 ml hexane and 1 ml ether; 5·40 g (77%), m.p. 77—79°C. Analytical sample, m.p. 78—79°C (ether–hexane). IR spectrum: 691, 747, 755 (5 and 4 adjacent Ar—H), 912, 1 233, 1 703, 2 610, 2 640, 2 790, infl. 3 130 (COOH), 1 466, 1 473, 1 478, 1 584 cm^{-1} (Ar). ^1H NMR spectrum: δ 11·20 (bs, 1 H, COOH), 7·00—7·60 (m, 9 H, ArH), 4·48 (q, J = 7·0 Hz, 1 H, ArCHCO), 1·40 (d, J = 7·0 Hz, 3 H, CH_3). Lit.[43], m.p. 76—77·5°C (the compound was prepared by a different method).

2-Methyl-2-(2-phenylthiophenyl)propionic Acid (*XIX*)

A solution of 20 g *XVII* and 20 g KOH in 80 ml ethylene glycol was refluxed for 15 h (bath of 200°C). After cooling the mixture was dissolved in 1 l water, the solution was washed with benzene and acidified with 80 ml hydrochloric acid. The product was extracted with benzene, the extract was dried ($MgSO_4$) and evaporated; 16·5 g (75%), m.p. 170—175°C. Analytical sample, m.p. 174—175°C (benzene). Mass spectrum, *m/z*: 272 (M^+ corresponding to $C_{16}H_{16}O_2S$), 228, 213, 91 (base peak, tropylium!). IR spectrum: 700, 757, 772 (5 and 4 adjacent Ar—H), 930, 1 268, 1 285, 1 691, 2 605, 2 665, 2 775, infl. 3 140 (COOH), 1 491, 1 567, 1 586, 1 599, 3 030, 3 040, 3 060 cm^{-1} (Ar). ^1H NMR spectrum: δ 11·80 (bs, 1 H, COOH), 6·60—7·60 (m, 9 H, ArH), 2·20 and 1·95 (2 s, 3 + 3 H, 2 C—CH_3). For $C_{16}H_{16}O_2S$ (272·4) calculated: 70·56% C, 5·92% H, 11·77% S; found: 70·80% C, 5·90% H, 12·06% S.

2-Methyl-2-(2-phenylsulfinylphenyl)propionic Acid (*XX*)

A solution of 5·85 g *XVII* in 25 ml ethanol was treated with 15 ml 50% aqueous KOH and the mixture was stirred and refluxed for 15 h. Ethanol was distilled off, the residue was diluted with 80 ml water and extracted with 50 ml benzene. The benzene layer was washed with 5% KOH and water, dried and evaporated *in vacuo*. The residue (4·66 g) is a neutral substance not containing the starting *XVII* (thin-layer chromatography) which was considered to be the crude 2-methyl-2-(2-phenylthiophenyl)propionamide. It was dissolved in 200 ml acetic acid, the solution was treated with 7·5 ml H_2SO_4 and then under stirring with a solution of 5·9 g $NaNO_2$ in 25 ml water. The mixture was allowed to stand overnight, heated for 30 min to 100°C, cooled, treated with a solution of 4·4 g $NaNO_2$ in 15 ml water and heated for 30 min to 100°C. Acetic acid was evaporated *in vacuo*, the residue was diluted with 200 ml water and extracted with benzene. The extract was washed with 180 ml 5% NaOH, the aqueous layer was acidified with hydrochloric acid and the product extracted with benzene. Evaporation of the extract gave a residue which crystallized after treatment with 6 ml ethanol; 0·88 g (18%) yellow prisms, m.p. 215—216°C. Analytical sample, m.p. 216—217°C (ethanol). IR spectrum: 685, 740, 748, 760 (5 and 4 adjacent Ar—H), 925, 1 220, 1 709, 2 560, 2 600, 2 705, 2 745, 2 780, infl. 3 100 (COOH), 992, 1 005 (ArSOAr'), 1 480, 1 565, 1 580, 1 590, 3 030 cm^{-1} (Ar). Polarographic reduction in ethanolic 0·5M-HCl (towards a saturated calomel electrode) $E_{1/2}$ = −0·91 V (SO). ^1H NMR spectrum ($C^2H_3SOC^2H_3$): δ 7·20—7·70 (m, 9 H, ArH), 1·65 and 1·60 (2 s, 3 + 3 H, 2 C—CH_3). For $C_{15}H_{16}O_3S$ (288·3) calculated: 66·64% C, 5·59% H, 11·12% S; found: 66·98% C, 5·97% H, 10·90% S.

11-Methyldibenzo[*b,f*]thiepin-10(11*H*)-one (*XXI*)

A) A mixture of 4·80 g *XVIII* and 50 g polyphosphoric acid (from 25 g P_2O_5 and 25 g 85% H_3PO_4) was stirred and heated for 3 h to 115—120°C, after cooling decomposed with 100 ml water and extracted with warm benzene. The extract was filtered, washed with 5% NaOH, dried with K_2CO_3 and evaporated. The residue (4·15 g) was dissolved in 10 ml benzene and chromatographed on 120 g Al_2O_3. Benzene eluted first 2·12 g (47%) homogeneous oil which distilled at 10 Pa

from a bath heated to 120—125°C. Mass spectrum, *m/z* (%): 240 (M^+ corresponding to $C_{15}H_{12}OS$, 26%), 225 (49, $C_{14}H_9OS$), 224 (55), 208 (17, $C_{15}H_{12}O$), 198 (100, $C_{13}H_{10}S$), 179 (10), 166 (27, $C_{13}H_{10}$). IR spectrum (film): 695, 730, 750, 792 (5 and 4 adjacent Ar—H), 1 028, 1 140 (C—O of CO), 1 370 (C—H of CH_3), 1 447, 1 493, 1 590, 3 025 (Ar), 1 710 cm^{-1} (COAr). For $C_{15}H_{12}OS$ (240·3) calculated: 74·96% C, 5·04% H, 13·34% S; found: 74·91% C, 5·07% H, 13·50% S. Lit.[27], b.p. 148—150°C/2·7 Pa and m.p. 62—64°C.

The following fraction of the chromatography, eluted still with benzene, yielded 100 mg thioxanthone (*XXII*), m.p. 213—215°C (benzene). Mass spectrum, *m/z* (%): 212 (M^+ corresponding to $C_{13}H_8OS$, 100%), 197 (1), 184 (55, M—28). UV spectrum: λ_{max} 254·5 nm (log ε 4·65), 374 nm (3·89), inflexes at 284 nm (3·72) and 296 nm (3·57). IR spectrum: 731 (4 adjacent Ar—H), 1 482, 1 590 (Ar), 1 643 cm^{-1} (ArCOAr). Lit.[34,35], m.p. 209°C, and 214—215°C, respectively.

B) A mixture of 5·0 g *XVIII* and 120 g polyphosphoric acid (from 65 g P_2O_5 and 55 g 88% H_3PO_4) was stirred and heated to 60—80°C for 24 h, after cooling decomposed with 400 ml water, shaken with 200 ml benzene and the heterogeneous system was filtered. The benzene layer of the filtrate was separated, washed with 5% NaOH and water, dried with K_2CO_3 and evaporated *in vacuo*. The residue (2·45 g) deposited on standing 150 mg of thioxanthone (*XXII*), m.p. 214—215°C (*cf.* under *A*). The residue was chromatographed on 60 g Al_2O_3. Benzene eluted 1·27 g less polar oil and further 200 mg thioxanthone. The oil was rechromatographed on 25 g Al_2O_3; the least polar fraction obtained by elution with benzene crystallized, 300 mg thioxanthene (*XXIII*), m.p. 128·5—129·5°C (benzene–light petroleum). Mass spectrum, *m/z* (%): 198 (M^+ corresponding to $C_{13}H_{10}S$, 75%), 197 (100), 165 (23), 152 (10), 99 (10), 98 (10). ^{1}H NMR spectrum: δ 7·00—7·50 (m, 8 H, ArH), 3·81 (s, 2 H, $ArCH_2Ar$). Lit.[35,36], m.p. 124—128°C, and 128°C, respectively.

C) A mixture of 5·0 g *XIX* and 120 g polyphosphoric acid (like under *B*) was stirred and heated to 100°C for 30 h. After decomposition with 500 ml water, the separated product was extracted with benzene. Processing of the extract gave only 1·77 g inhomogeneous residue (mixture of at least three neutral components). It was chromatographed on 50 g Al_2O_3. The least polar fraction which was eluted with a 3 : 1 mixture of light petroleum and benzene (400 mg) was rechromatographed on 60 g Al_2O_3. The first fractions, eluted with light petroleum, gave 25 mg, m.p. 76 to 78°C (light petroleum), considered to be 10-methyldibenzo[*b,f*]thiepin (*XXIV*). Mass spectrum, *m/z*: 224 (M^+ corresponding to $C_{15}H_{12}S$, 100%), 223, 210. ^{1}H NMR spectrum: δ 7·10—7·90 (m, 9 H, ArH and Ar—CH=C), 2·41 (s, 3 H, =C—CH_3). For $C_{15}H_{12}S$ (224·3) calculated: 80·33% C, 5·39% H; found: 80·30% C, 5·17% H. Lit.[27,38], m.p. 51—52°C.

The preceding substance was immediately followed (in the mentioned rechromatography using still light petroleum as eluent) by 120 mg of a further crystalline compound, m.p. 174 to 175°C (benzene–light petroleum), to which the structure of 9-methylenethioxanthene (*XXV*) is ascribed. Mass spectrum, *m/z*: 210 (M^+ corresponding to $C_{14}H_{10}S$), 178, 165, 105. For $C_{14}H_{10}S$ (210·2) calculated: 79·98% C, 4·79% H, 15·22% S; found: 79·57% C, 4·84% H, 14·98% S. The literature[39] describes *XXV* as a yellow oil solidifying bellow —17°C but then melting only at 45°C.

The main product was obtained in the original chromatography by elution with a 3 : 1 mixture of light petroleum and benzene as a slightly more polar component than the preceding two compounds; 0·75 g (17%) oil boiling at 10 Pa from a bath heated to 120—130°C. It was identified by means of analysis, mass spectrum and IR spectrum as *XXI*, described under *A*.

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