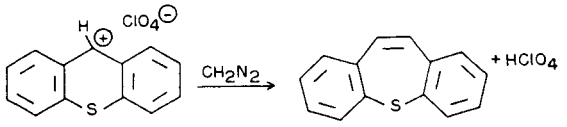
Department of Chemistry, Massachusetts Institute of Technology

Reaction of Thioxanthylium Perchlorate with Diazomethane.

Helmut Seidl and Klaus Biemann

The reaction of thioxanthylium perchlorate with diazomethane was investigated. Depending on the reaction conditions, seven compounds (II, III, V, VI, VIII, IX, and X) are formed which were identified on the basis of spectral data (mainly mass spectra) and chemical reactions. A synthesis was worked out (reaction of compound VII with boron trifluoride) in which dibenzo[*b*,*f*]thiepine (VIII) is formed as major product (55%).

In the course of mass spectrometric investigations described elsewhere (1), a sample of dibenzo[b,*f*]-thiepine, VIII (2-4) was required. By reaction of thioxanthylium perchlorate (I) with diazomethane, Whitlock (4) had obtained VIII in 22% yield and this method was chosen for the preparation of this compound because it seemed to be straight forward in spite of the fact that there were no experimental details reported.



I VIII

Failure of the detection of any of the desired product VIII in our first attempts to repeat Whitlocks experiments led to a detailed investigation of this reaction, which turned out to be quite complex inasmuch as it produces up to six compounds in addition to VIII, in widely varying amounts, depending on the reaction conditions. Based on these results, which will be discussed in this paper, a synthesis of VIII was worked out (reaction of isopropyl ether VII with boron trifluoride) in which this compound is formed as a major product (55%). Furthermore, since most of the byproducts are derivatives of 10,11-dihydrodibenzo[*b*,*f*]thiepine, a class of compounds which has recently gained attention because of their neurotropic and psychotropic activity (3), the reaction sequences outlined in this paper may be of use in the preparation of other members of this series.

Two factors were found to have a decisive influence on the products formed in the reaction of thioxanthylium perchlorate with diazomethane: the reaction time and the purity of the solvent, particularly the water content of the ether used as a solvent.

First, the formation of the products as a function of the reaction time shall be discussed. Addition of an ethereal solution of diazomethane to a suspension of thioxanthylium perchlorate in ether at 0° initiated an immediate reaction: the red salt dissolved rapidly. After the addition of diazomethane had been completed (persisting yellow color of the solution) the reaction mixture was stirred for an additional 15 minutes. Evaporation of the solvent yielded a yellow oil which could be separated into five components by thin layer chromatography.

The substance with the lowest R_f value, a colorless solid isolated in 8% yield, was identified by its mass spectrum as 10-hydroxy-10,11-dihydrodibenzo[*b*,*f*]thiepine (V). The molecular ion, m/e 228, loses a hydroxyl group in the form of water to give an abundant fragment at m/e 210 corresponding to the molecular weight of dibenzo[*b*,*f*]thiepine whose preparation and mass spectrum will be discussed later. Structure V was confirmed by comparison of the melting point with that given in the literature (3), by the n.m.r. spectrum and by chemical conversion of V into dibenzothiepine on treatment with boron trifluoride in acetic anhydride.

The component with the next higher R_f value, isolated in 14% yield, had a molecular weight of 212 and was identified as thioxanthone (II) by mixture melting point and comparison of its spectral data (UV, IR, NMR and MS) with those of an authentic sample.

As the third component, in order of increasing R_f values, a colorless crystalline substance was obtained in 2% yield. Its infrared spectrum shows a strong carbonyl band at 1675 cm^{-1} in addition to a broad OH-peak at 3600 cm^{-1} indicating a highly conjugated ketone. This is in agreement with the mass spectrum which shows loss of CO and COH from the molecular ion (m/e 226) and leads to the conclusion that the compound in question is 10,11-dihydrodibenzo[*b*,*f*]thiepin-10-one (X). This was confirmed by comparison of melting point and infrared spectrum of compound X with data recently published (3) for this substance.

The structure of the fourth fraction, a colorless oil isolated in 5% yield, was derived from its mass spectrum. Loss of methanol from the molecular ion (m/e 242) gives rise to the most intense peak

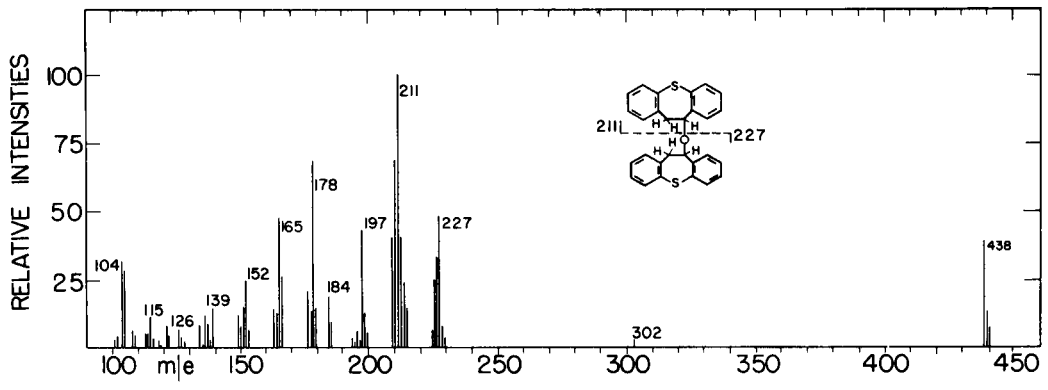
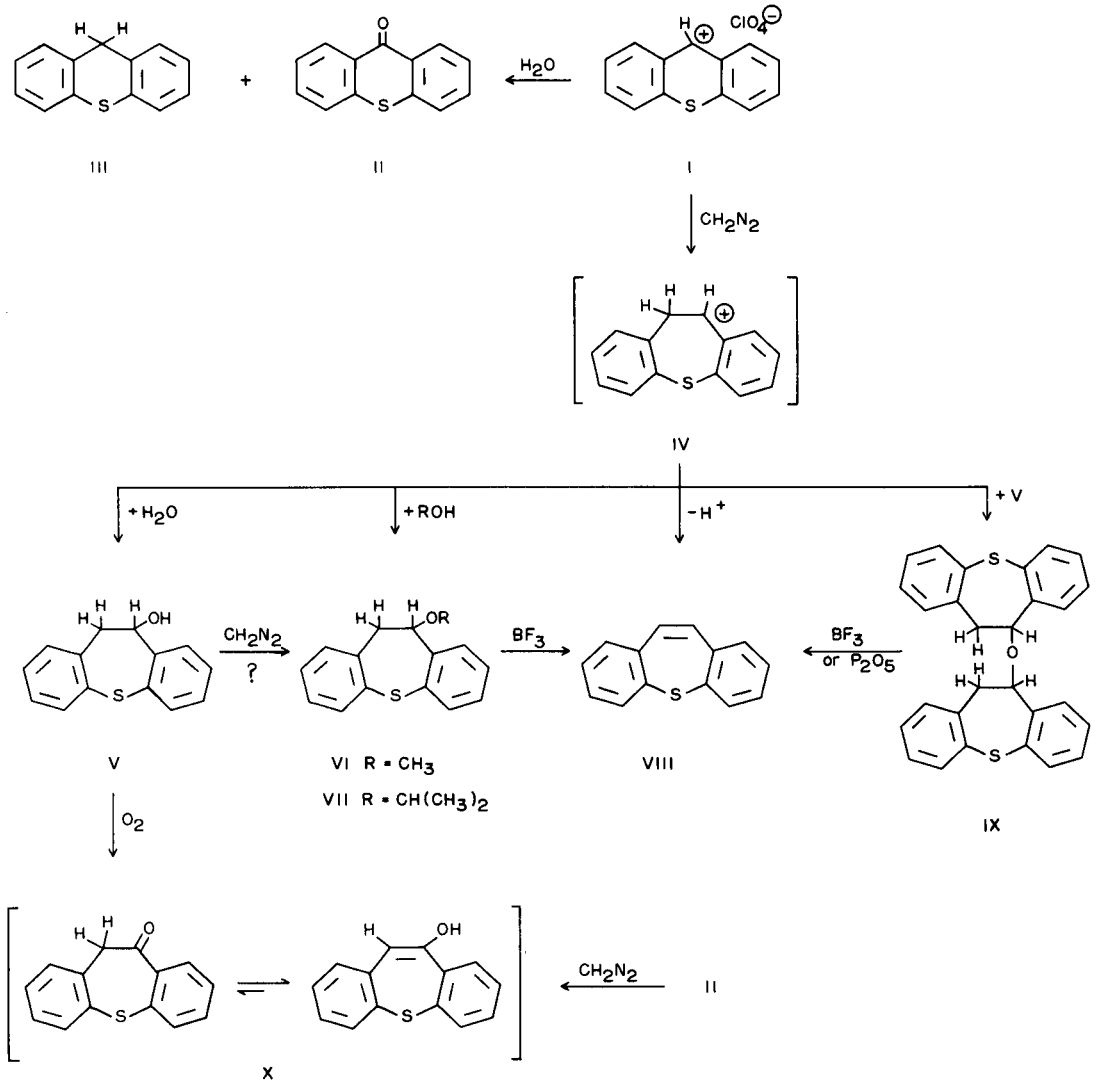


Figure I. Mass spectrum of di-(10,11-dihydrodibenzo[*b*,*f*]thiepinyl-10)-ether (IX). Only peaks are listed with intensities above 0.5% of total ionization.



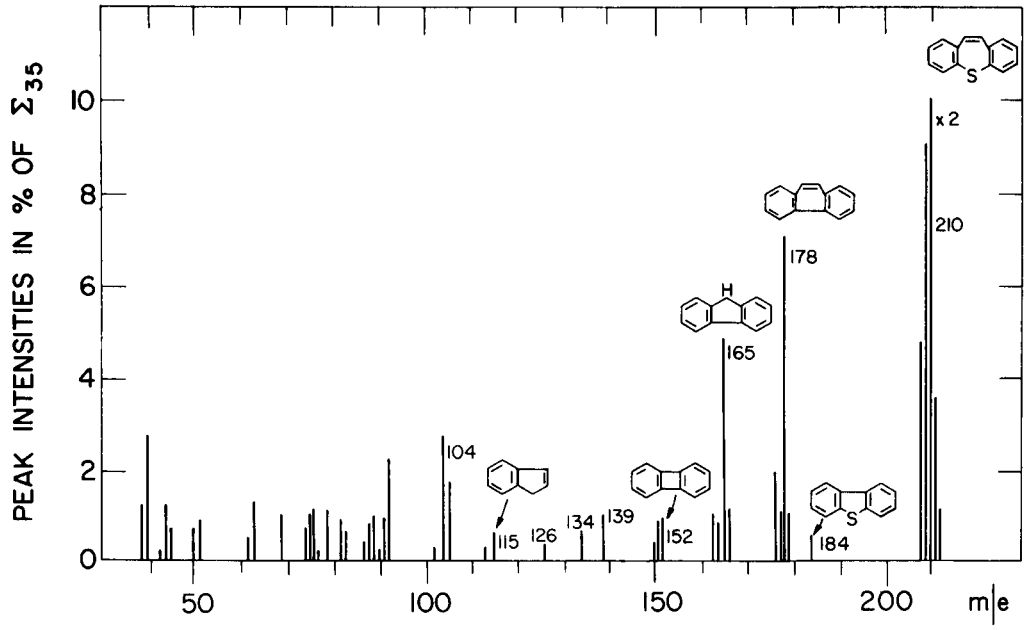


Figure II. Mass spectrum of dibenzo[*b*,*f*]thiepine (VIII). Only peaks are listed with intensities above 0.3% of total ionization.

at m/e 210, corresponding to the molecular weight of dibenzothiepine. The remainder of the spectrum, with the exception of two additional peaks at m/e 197 and 194, resembles that of dibenzothiepine. This fragmentation pattern can be rationalized only in terms of 10-methoxy-10,11-dihydrodibenzo[*b*,*f*]thiepine (VI), a compound not previously described in the literature. Structure VI was further supported by analysis ($C_{15}H_{14}OS$), n.m.r. spectrum (see experimental section) and chemical conversion into dibenzothiepine by heating compound VI with boron trifluoride in acetic anhydride.

From the fifth fraction, the least polar component of the reaction mixture, colorless crystals were isolated in 7% yield. Osmometric molecular weight determination (found 470) and microanalysis (found $C_{28}H_{22}OS_2$) gave evidence for a dimeric product containing only one oxygen atom. Since an OH or a carboxylic function could not be detected in the infrared spectrum, the oxygen was ascribed to an ether bond (IR absorption at 1085 cm^{-1}). On the basis of these data structure IX was proposed for this compound which was further corroborated by the n.m.r. spectrum which contains only three kinds of protons: the aromatic protons at 7.32 ppm., the tertiary hydrogen atoms at 5.77 ppm., and the methylene groups at 3.47 ppm., in the correct ratio of 16:2:4. Structure IX was further supported by the mass spectrum (Figure I). An intense molecular peak is present at m/e 438. Cleavage of the ether bond gives rise to the dihydrodibenzothiepinylium ion (m/e 211) and the corresponding oxygen containing fragment (m/e 227) which eliminates CH_2O to give a fragment at m/e 197. Assignments for the ions at m/e 184, 178, 165, 152 and 139 will be made later in connection with the mass spectrum of dibenzothiepine. A very striking aspect of the mass spectrum of compound IX is the absence of fragments (with exception of an unassigned fragment at m/e 302 of very low abundance) between the molecular ion (m/e 438) and the first fragment of about half the molecular weight (m/e 227). Such a situation could induce one to terminate the recording of the mass spectrum too early, thus missing the molecular ion. Possible errors resulting from this can naturally be eliminated by routinly measuring a spectrum up to a mass region of about twice the expected molecular weight and by closely inspecting the mass spectrum for doubly charged ions. In the spectrum of compound IX the doubly charged molecular ion can be found at m/e 219, recognized by its isotope peak at 219.5. If substance IX is not introduced directly into the ion source but heated into the reservoir of the inlet system it decomposes thermally to 10-hydroxy-10,11-dihydrodibenzothiepine (V) and dibenzothiepine (VIII) as indicated by the abundance of their molecular ions (m/e 228 and 210, respectively). The true molecular ion (m/e 438) is very weak or can be absent altogether, depending on the heating conditions.

Chemical evidence for structure IX involved cleavage of the ether bond with boron trifluoride in acetic anhydride which, probably via *O*-acetyl-10,11-dihydrodibenzothiepin-10-ol as unstable inter-

mediate, leads to dibenzothiepine. Conversion of IX into dibenzothiepine can also be achieved by boiling IX with phosphorus pentoxide in xylene. The possibility that this is again merely a thermal reaction is excluded by heating IX in xylene alone which leads to quantitative recovery of unchanged starting material.

It is of interest to note that dibenzo[*b*,*f*]thiepine, the desired product of the reaction of thioxanthylium perchlorate with diazomethane, could have been formed only to an amount insufficient for detection by thin layer chromatography (using UV light or iodine vapor).

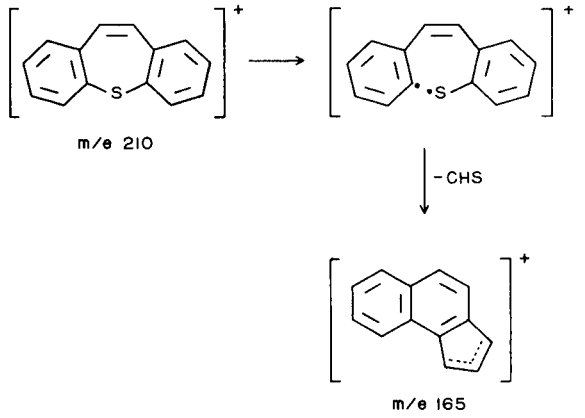
The formation of all products discussed above can be summarized as shown in Scheme I. The key intermediate is the dihydrodibenzo[*b*,*f*]thiepine carbonium ion IV which reacts with water to alcohol V and, subsequently, with V to yield the dimeric ether IX. 10-Methoxy-10,11-dihydrodibenzothiepine (VI) can, in principle, be formed in two ways: either by methylation of V with excess of diazomethane, or by reaction of IV with methanol. Since pure 10-hydroxy-10,11-dihydrodibenzothiepine (V) could not be methylated with diazomethane in ether (see experimental section and ref. 5) and methanol is absent in the ether used as solvent we have to assume that either one of the reaction partners (carbonium ion IV ?) displays a catalytic effect on the methylation of V with diazomethane, or that methanol is formed during the reaction, for instance by decomposition of methyl perchlorate, a possible reaction product of diazomethane and perchloric acid.

Dibenzo[*b*,*f*]thiepin-10-one (X) could be formed either by autoxydation of V (analogous to the autoxydation of 10-thioxanthenol (6) or by diazomethane ring enlargement (7) of thioxanthone (II), a product of hydrolysis and autoxydation of thioxanthylium perchlorate (see below). Since the amount of thioxanthone decreases with the reaction time (see experimental section) the latter way of formation seems to be more likely.

The fact that IV does not lose a proton to a considerable extent during the initial 15 minutes, after the addition of diazomethane has been completed, to give dibenzo[*b*,*f*]thiepine (VIII), implies that carbonium ion IV is a relatively stable, long-lived species. If this is the case the yield of VIII should be improved by a longer reaction time. Furthermore, it should be possible to trap the ion IV, for instance by addition of alcohol, after several hours or even days. Both assumptions were supported by the products formed on quenching aliquots of the reaction mixture with isopropyl alcohol after various time intervals. The expected products, dibenzothiepine (VIII) and the isopropyl ether VII could indeed be isolated, in addition to a third newly detected component, thioxanthene (III).

In agreement with this hypothesis the amount of dibenzothiepine formed depends on the reaction time. The yield increases rapidly during the first 20 hours (0-20%) and then levels off to about 40% after several days. This is obviously the reason for our initial failure to obtain the desired product VIII in a reasonable yield.

The mass spectrum of dibenzo[*b*,*f*]thiepine (Figure II) shall be discussed briefly, particularly as its major fragments are also present in the spectra of all dibenzo[*b*,*f*]thiepine and dihydrodibenzothiepine derivatives. The fragments of highest mass (m/e 184 and 178) are formed by loss of acetylene or sulfur, respectively. The peak at m/e 152 is due to loss of acetylene together with sulfur from the molecular ion. The peak at m/e 165 is also present in the spectra 2,3:6,7-dibenzosuberene, dibenzo[*b*,*f*]oxepine and dibenzo[*b*,*f*]azepine (containing CH_2, O, or NH in place of S) and, therefore, must have been formed by loss of the heteroatom (S) together with CH from the molecular ion as indicated in the following scheme:

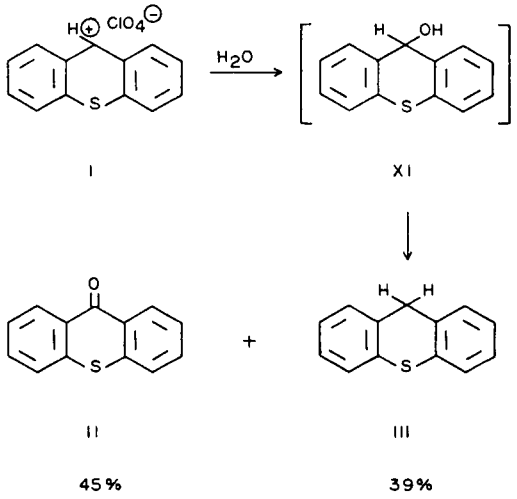


Elimination of acetylene from the fragments at m/e 165 and 152 yields ions at m/e 139 and 126. The indene ion, a species characteristic for most condensed aromatic systems, gives rise to the peak at m/e 115. The peaks at m/e 105 and 104 correspond to C_8H_9 and C_8H_8 ions for which structure assignments lack any basis.

The yield of the isopropyl ether VII, not previously described in the literature, remains relatively constant during the first 20 hours (average of 30%) and decreases slightly after 4 days (to about 20%). The structure of VII is corroborated by analysis, n.m.r. and mass spectrum. The molecular ion (m/e 270) loses the isopropyl group and isopropyl alcohol to give fragments at m/e 227 and 210, respectively, which have also been observed in the spectrum of the methyl ether VI. Treatment of VII with boron trifluoride in acetic anhydride eliminates isopropyl alcohol to yield dibenzothiepine. To ascertain that the isopropyl ether VII was indeed formed from carbonium ion IV and isopropyl alcohol, three separate control experiments were performed. The ethers VI and IX as well as the alcohol V were treated with isopropyl alcohol: in none of these

three experiments reaction took place and unchanged starting material was recovered.

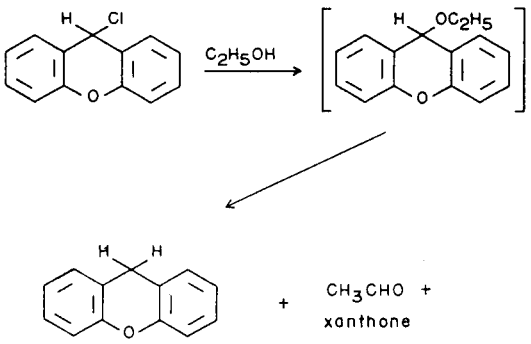
Thioxanthene (III) was recognized by its mass spectrum and identified by comparison with authentic material. Its formation, together with that of thioxanthone (II), seems to be due to hydrolysis of thioxanthylium perchlorate, the starting material, to thioxanthen-9-ol (XI) which disproportionates (8) to II and III. The ratio in which these compounds are formed was determined in a test experiment:



In this context another experiment must be mentioned here because its unexpected results imply another possible source for thioxanthene. Dry thioxanthylium perchlorate dissolves slowly in dry isopropyl alcohol under decolorization. Concentration of the reaction mixture and analysis by thin layer chromatography gives thioxanthene as major product, together with some thioxanthone:

$$\text{I} \xrightarrow{(CH_3)_2CHOH} 21\%\ \text{II} + 67\%\ \text{III}$$

This reaction is analogous to that of xanthylium chloride which is reduced by ethanol to xanthene, xanthone being isolated only in traces (9):



It now remains to discuss the origin of water and its influence on the formation of the products. As shown in Scheme I, products II, III, V, and IX require water for their formation. While thioxanthone (II), thioxanthene (III) and the alcohol V are most probably hydrolysis products due to chromatographic work-up (thin layer plate or column), the dimeric ether IX must be the reaction product of alcohol V and the carbonium ion IV. This requires that at least a small amount of the alcohol V is present in the reaction mixture due to water in the solvent. Although great care was taken to use anhydrous ether, to flame all reaction flasks and to protect them with drying tubes against moisture, the operation of transferring the ethereal diazomethane solution (dried 3 hours over potassium hydroxide pellets) to the reaction flask by means of a pipette provides enough water to form some IX via alcohol V. Only by working in a completely closed apparatus, pumping the diazomethane solution from the storage bottle through a thin tube into the reaction flask, it was possible to retard the formation of the ether IX. Compounds II, III and V, however, were still present, supporting our above mentioned explanation of hydrolysis during isolation.

Based on the knowledge of the structure and properties of all products formed it was now possible to modify the reaction of thioxanthylium perchlorate with diazomethane in any desired direction. If the ethers VI and VII are the products required, one has to add a mixture of methanol and isopropyl alcohol to the reaction mixture a short time after the diazomethane addition has been concluded. Thus, the carbonium ion IV is trapped as ether VI and VII before aromatizing by loss of a proton. On the other hand, since the ethers VI or VII can be converted to dibenzothiepine (VIII), a new synthesis of VIII is available. In this case the ether (*e.g.* VII) has not even to be isolated but can be converted directly to VIII by reaction with boron trifluoride in acetic anhydride. The advantage of using this reagent is that the undesired byproducts (V, VI and IX) are simultaneously converted to dibenzothiepine which, therefore, is formed as main product (55% yield).

EXPERIMENTAL

Melting points, determined on a Kofler hot-stage microscope, are uncorrected. The mass spectra were recorded on a CEC 21-103C mass spectrometer, equipped with a heated stainless steel inlet system operated at 150°; ionization potential 70 eV., ionizing current 50 $\mu\alpha$, temperature of the ion source 250°. The infrared spectra were measured on a Perkin-Elmer Model 237 spectrometer. A Varian Associates A-60 instrument was used for n.m.r. spectra.

Thioxanthylium Perchlorate (I).

Perchloric acid (70%, 10 ml.) was dropped slowly into a stirred suspension of 10 g. of thioxanthen-9-ol (6) in 100 ml. of ether at 0°. After warming up to room temperature, the red salt was collected on a funnel and washed several times with ether. Crystallization from acetic acid gave 7.5 g. (53%) of thioxanthylium perchlorate with m.p. 229-231° (dec.); reported (10) m.p. 229° (dec.).

Anal. Calcd. for $C_{13}H_9O_4SCl$: C, 52.62; H, 3.05; S, 10.81; Cl, 11.95. Found: C, 52.38; H, 3.05; S, 10.70; Cl, 12.44.

Reaction of I with Water.

Thioxanthylium perchlorate (I) (100 mg.) was stirred in 5 ml. of water for 5 hours. The organic material was extracted with methylene chloride and applied to a thin layer plate (Silica gel H, Merck; petroleum ether/benzene = 6/4 as moving phase). One fraction (smaller R_f value) was thioxanthone (32 mg., 45%, m.p. 214°), the other thioxanthene (26 mg., 39%, m.p. 129-130°).

Reaction of I with Isopropyl Alcohol.

Compound I (100 mg.) was stirred in 5 ml. of isopropyl alcohol for 1 hour. The red salt dissolved slowly with decolorization. After several minutes colorless needles crystallized from the solution. The reaction mixture was concentrated and analyzed by thin layer chromatography (Silica gel H, Merck; petroleum ether/benzene, 6/4, as moving phase). Fifteen mg. of thioxanthone (21%) and 45 mg. of thioxanthene (67%) were isolated and identified by mixture melting points.

Reaction of I with Diazomethane (15 Minute Reaction Time).

An ethereal solution of diazomethane, prepared (11) from 1 g. of nitrosomethyl urea and dried for 3 hours over potassium pellets (*ca.* 6.5 mmoles), was dropped slowly into a stirred suspension of 1.00 g. (3.4 mmoles) of thioxanthylium perchlorate (I) in 25 ml. of anhydrous ether at 0° over a period of 20 minutes. At this time the major part of the red salt had dissolved leaving only a small amount of unreacted perchlorate as a red gum, although the yellow color of the solution indicated an excess of diazomethane. After an additional 15 minutes of stirring at 0° the ethereal solution was decanted from the unreacted perchlorate (210 mg., 0.7 mmole) and concentrated *in vacuo*. The semicrystalline residue was dissolved in 6 ml. of methylene chloride and applied to 8 thin layer plates (8 x 8"; 0.8 mm layer of Silica gel H, Merck) and developed with petroleum ether/benzene (6/4). A small lane of each plate was exposed to iodine vapor and indicated 5 fractions. The corresponding fractions of all plates were combined, eluted with methylene chloride and concentrated. They are described here in order of increasing R_f values. Yields are calculated from reacted thioxanthylium perchlorate.

Fraction No. 1: 10-hydroxy-10,11-dihydrodibenzo[*b*,*f*]thiepine (V). Yield: 48 mg. (0.21 mmole, 8%); m.p. 99-100° after crystallization from cyclohexane. Reported (3) m.p. 100°.

MS: 228, 213, 210, 197, 195, 184, 178, 165, 152, 136, 121, 105 m/e.

NMR: 7.10-7.65 ppm. (mult., arom. H); 5.18-5.45 ppm. (quart., OH); 3.08-3.95 ppm. (2 quart., methylene H); 2.19 ppm. (sing., tert. H). Integrals 8:1:2:1.

Fraction No. 2: thioxanthone (II). Yield: 78 mg. (0.37 mmole, 14%). Colorless needles with m.p. 214-215° (from ethyl acetate). Identified by comparison with an authentic sample.

Fraction No. 3: 10,11-dihydrodibenzo[*b*,*f*]thiepin-10-one (X). Yield 12 mg. (0.05 mmole, 2%). Yellow crystals (from ethanol), m.p. 68-70°. Reported (3, 12) m.p. 72-73° and 68°, respectively.

MS: 226, 198, 197, 194, 193, 165, 152, 139, 121 m/e.

IR (CCl_4): 3600, 3075, 1680, 1590, 1475, 1450, 1430, 1285, 1230, 1145, 1115, 1080, 1040, 1019 cm^{-1}.

Fraction No. 4: 10-methoxy-10,11-dihydrodibenzo[*b*,*f*]thiepine (VI). Yield: 32 mg. (0.13 mmole, 5%) of a colorless oil. B.p. 170° bath-temp./0.6 mm. For preparation of larger amounts see later.

Mol. Weight (osmometric in benzene): 237.

Anal. Calcd. for $C_{15}H_{14}OS$: C, 74.50; H, 5.82; S, 13.20. Found: C, 74.60; H, 5.97; S, 13.02.

IR (CCl_4): 3050, 2915, 2810, 1449, 1420, 1200, 1109, 1058, 1035, 977, 671 cm^{-1}.

NMR (CCl_4): 7.18 ppm. (mult., arom. H); 5.22 ppm. (quart., tert. H); 3.38 ppm. (dubl. ?, methyl group); 3.33 ppm. (doubl. ?, methylene H). Integrals 8:1:3:2.

MS: 242, 227, 210, 197, 194, 184, 179, 178, 165, 152, 139, 134, 121, 115, 105 m/e.

Fraction No. 5: di-(10,11-dihydrodibenzo[*b*,*f*]thiepinyl-10)-ether (IX). Yield: 85 mg. (0.19 mmole, 7%) of colorless crystals, m.p. 175-177° (sintering from 155°) after crystallization from ethyl acetate.

Mol. Weight (osmometric in benzene): 470.

Anal. Calcd. for $C_{28}H_{22}OS_2$: C, 76.80; H, 5.06; S, 14.57. Found: C, 76.77; H, 5.03; S, 14.54.

IR (CCl_4): 3052, 2995, 2900, 1460, 1425, 1200, 1086, 720 cm^{-1}.

NMR ($CDCl_3$): multiplets at 7.32, 5.77, and 3.47 ppm. Integr. 8:1:2.

MS: 438, 227, 211, 197, 184, 178, 165, 152, 134, 121, 115, 105 m/e.

Reaction of V with Boron Trifluoride.

Compound V (50 mg.) was dissolved in 3 ml. of acetic anhydride and treated at 0° with 10 drops of boron trifluoride-ethyl ether complex. After storage for 24 hours at room temperature the reaction mixture was poured into water, stirred for 1 hour, extracted with methylene chloride, washed with a sodium bicarbonate solution and water, and dried over magnesium sulfate. Separation on a thin layer plate (Silica gel H, Merck; petroleum ether/benzene, 6/4, as moving phase) gave two fractions: 16 mg. (35%) of dibenzothiepine (larger R_f value, rusty brown UV fluorescence) with m.p. 86° after crystallization from methanol, and 10 mg. of starting material V (20%). Dibenzothiepine was identified by comparison with a sample prepared independently (2).

Reaction of V with Diazomethane.

Pure alcohol V (100 mg.), dissolved in 4 ml. of anhydrous ether, was treated at 0° with an ethereal solution of diazomethane (large excess). After standing for 1 hour at 0° and 20 hours at room temperature the ether was evaporated and the residue subjected to thin layer chromatography. Besides the starting material V no other compound could be detected on the plate.

Reaction of VI with Boron Trifluoride.

Methyl ether VI (70 mg.) was treated with boron trifluoride in acetic anhydride as described for compound V: 54 mg. of dibenzothiepine (90%), m.p. 85-87° after crystallization from methanol.

Reaction of IX with Boron Trifluoride.

Dimeric ether IX (50 mg.) was treated with boron trifluoride in acetic anhydride as described for compound V. Yield: 32 mg. (68%) of dibenzothiepine, m.p. 84-87°.

Reaction of IX with Phosphorus Pentoxide in Xylene.

Ether IX (50 mg.) and 1 g. of phosphorus pentoxide in 10 ml. of xylene were refluxed for 30 minutes. The cold reaction mixture was poured into ice water, extracted with chloroform, washed with sodium bicarbonate solution and dried over magnesium sulfate. After concentration of the solution the residue was admitted to a short chromatography column (aluminum oxide, neutral, Woelm, act. I; petroleum ether/benzene, 5/1, as eluent). The middle fraction gave 33 mg. of a semicrystalline substance. Crystallization from methanol yielded 23 mg. of dibenzothiepine (50%, m.p. 85-87°). In a test experiment IX was heated in xylene alone for 30 minutes. Work-up as described above gave pure starting material in about 95% yield.

Reaction of I with Diazomethane (Addition of Isopropyl Alcohol after Various Time Intervals).

Thioxanthylium perchlorate (I) (3.0 g.) was treated with diazomethane (prepared from 3 g. of nitrosomethyl urea) as described above. At various time intervals (see Table I) 10 ml. samples were withdrawn from the reaction mixture (80 ml.), added to 5 ml. of isopropyl alcohol, stored for 1 hour at room temperature and concentrated. Each sample was then separated on thin layer plates into 8 fractions: No. 1, 2, 3, 4, 4a, 5, 6, and 7 (in order of increasing R_f values). Fractions No. 1, 2, 3, 4, and 5 are identical with those already described above. The newly detected fractions (in iodine vapor) No. 4a, 6, and 7 will be described below. The yields are summarized in Table I.

TABLE I

Yields of All Compounds Formed in the Reaction of Thioxanthylium Perchlorate with Diazomethane as Function of the Reaction Time

	% yield of							
fraction no.	1	2	3	4	4a	5	6	7
compound	V	II	X	VI	VII	IX	VIII	III
5 hours	5	15	2	7	29	5	5	10
10 hours	6	8	1	6	33	3	8	8
20 hours	3	8	2	4	22	3	20	3
2 days					25		26	
3 days					22		27	
4 days					20		42	

Fraction No. 4a: 10-isopropoxy-10,11-dihydrodibenzo[*b*,*f*]thiepine (VII). Colorless oil with b.p. 180-185° bath temp./0.6 mm. For preparation

of larger amounts see later.

Anal. Calcd. for $C_{17}H_{18}OS$: C, 75.52; H, 6.70; S, 11.86. Found: C, 75.26; H, 6.72; S, 11.81.

IR (CCl_4): 3050, 2955, 1450, 1420, 1360, 1325, 1141, 1119, 1079, 1050, 1035, 945, 670 cm^{-1}.

NMR (CCl_4): 7.10 ppm. (mult., arom. H); 5.45 ppm. (quart., tert. H); 3.62 ppm. (mult., tert. isoprop. H); 3.00 ppm. (mult., methylene H); 1.19 and 1.08 ppm. (methyl groups, sing.). Integration 8:1:1:2:3:3.

MS: 270, 227, 210, 197, 195, 184, 178, 165, 152, 136, 121 m/e.

Fraction No. 6: dibenzo[*b,f*]thiepine (VIII). Yellow crystals from methanol, m.p. 87-88°. Reported (2) m.p. 89-90°. Identified by mixture m.p. and comparison of its physical properties with those of an authentic sample (2).

MS: See Figure II.

Fraction No. 7: thioxanthene (III). Colorless needles from ethyl acetate, m.p. 129-130°. Identification by comparison with an authentic sample.

MS: 198, 197, 165, 152, 139, 127, 126, 121, 115 m/e.

Reaction of VII with Boron Trifluoride.

Isopropyl ether VII (100 mg.) was dissolved in 4 ml. of acetic anhydride and treated with 10 drops of boron trifluoride at room temperature. After storage for 24 hours at room temperature, the reaction mixture was poured into water, extracted with methylene chloride, washed with sodium bicarbonate solution and dried over magnesium sulfate. Concentration of the solution gave 75 mg. (98%) of crude dibenzothiepine, m.p. 84-87° after crystallization from methanol.

Treatment of V with Isopropyl Alcohol.

Alcohol V (20 mg.) was dissolved in 3 ml. of isopropyl alcohol. After standing for 2 hours at room temperature the isopropyl alcohol was removed *in vacuo*. The mass spectrum of the remaining oil was identical with that of pure V.

Treatment of VI with Isopropyl Alcohol.

Ether VI (20 mg.) was dissolved in 3 ml. of isopropyl alcohol and stored at room temperature for 20 hours. Evaporation of the solvent gave pure starting material VI as shown by its mass spectrum.

Treatment of IX with Isopropyl Alcohol.

Dimeric ether IX (20 mg.) and 3 ml. of isopropyl alcohol were refluxed for 30 minutes. The solvent was evaporated *in vacuo* and the residue analyzed by mass spectrometry. Only unchanged starting material IX could be detected.

Reaction of I with Diazomethane (Methyl Ether VI and Isopropyl Ether VII as Main Products).

Thioxanthylium perchlorate, I (5.00 g., 16.8 mmoles), suspended in 50 ml. of ether, was treated at 0° with an ethereal solution of diazomethane, prepared from 5 g. of nitrosomethyl urea. After 2 hours of stirring at 0° the ether solution was decanted from unreacted perchlorate (1.0 g., 3.3 mmoles) and concentrated. Five ml. of methanol and 5 ml. of isopropyl alcohol were added to the residue. This caused immediate separation of a yellow oil which solidified on standing at 0° for 12 hours (1.3 g.). Column chromatography (neutral aluminum oxide, Woelm, act. I; petroleum ether/benzene, 1/1, as eluent) revealed a mixture of 310 mg. (0.7 mmole, 5%) of dimeric ether IX and 440 mg. (2.1 mmoles, 15%) of thioxanthone (II). The alcoholic solution was concentrated to give 3.1 g. of a brown oil which was chromatographed on Silica gel H, (Merck, 20 g.). Elution with petroleum ether/benzene (100/7) gave as first fraction 0.30 g. (1.4 mmoles, 10%) of dibenzothiepine (m.p. 87-88° after crystallization from methanol) and as a second fraction 1.10 g. (4.0 mmoles, 30%) of crude isopropyl ether VII which was purified by distillation (0.60 g., b.p. 180-185° bath temp./0.6 mm). Elution of the column with diethyl ether gave 0.70 g. (3.0 mmoles, 21%) of crude methyl ether VI which was subjected to distillation: 0.55 g. of a colorless oil with b.p. 170° bath temp./0.6 mm.

Reaction of I with Diazomethane (Dibenzo[*b,f*]thiepine as Main Product).

An ethereal diazomethane solution, prepared from 3 g. of nitrosomethyl urea, was dropped slowly into a stirred suspension of 3.00 g. (10.1 mmoles) of perchlorate I in 50 ml. of ether at 0°. After 30 minutes of stirring at 0° the ether solution was decanted from undissolved material (hydrolyzed to a mixture of thioxanthone and thioxanthene, corresponding to 2.6 mmoles of starting material) into 40 ml. of isopropyl alcohol. After standing for 3 hours at room temperature, the reaction mixture was concentrated *in vacuo*, dissolved in 20 ml. of acetic anhydride and treated with 2 ml. of boron trifluoride diethyl ether complex at 0°. The reaction mixture was stored for 12 hours at room temperature, poured into water and stirred for 1 hour. The separated oil was extracted with methylene chloride, washed with a 5% sodium carbonate solution and water and dried over magnesium sulfate. The solvent was evaporated *in vacuo* and the residue dissolved in 2 ml. of methylene chloride and subjected to column chromatography (17 g. of neutral aluminum oxide, Woelm, act. I). After a small fraction of a semicrystalline material (30 mg.) pure dibenzothiepine (VIII, 0.86 g., 55%, m.p. 84-86° after crystallization from methanol) was the only compound which could be eluted with petroleum ether/benzene (10/1; 150 ml.).

Acknowledgment.

This work was supported by a research grant from the National Science Foundation (GP 3734). We wish to thank Dr. I. Lengyel for helpful discussion concerning the structure of compound IX.

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Received March 6, 1967 Cambridge, Mass. 02139