REACTION OF SOME 3-(PHENYLTHIOARYL)PROPIONIC ACIDS WITH POLYPHOSPHORIC ACID; FORMATION OF 2*H*-CYCLOPENTA[*k,l*]THIOXANTHENES*

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Received November 21st, 1978

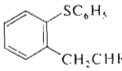
The cyclization of 3-[2-(phenylthio)phenyl]propionic acid (*I*) with polyphosphoric acid gave equal amounts of 4-(phenylthio)indanone (*III*) and 2*H*-cyclopenta[*k,l*]thioxanthene (*VI*), accompanied with a small amount of the macrocyclic diketone *V*. Compound *VI* was evidently formed *via* the cation *XII* and 7-(phenylthio)indanone (*X*) which was quantitatively dehydrocyclized. Similar cyclization of the isomeric acid *XIIIa* yielded 5-(phenylthio)indanone (*XVIII*) as the main product; formation of *VI* could be detected only chromatographically. Cyclization of 3-[2-chloro-5-(phenylthio)phenyl]propionic acid (*XIIIb*) gave 3-chloro-2*H*-cyclopenta[*k,l*]-thioxanthene (*VII*) as the predominant product. From the by-products formed, only 4-chloro--7-(phenylthio)indanone (*XI*) could be identified, being the precursor of compound *VII*. Treatment of thioxanthene-9-acetic acid (*XXII*) with polyphosphoric acid resulted in a cleavage with thioxanthone (*XXIII*) and thioxanthene (*XXIV*) as the main products.

Some time ago, our team reported in a preliminary manner[1] about the synthesis of 3-chloro-5-(4-methylpiperazino)-6,7-dihydro-5*H*-dibenzo[*b,g*]thiocin, *i.e.* a homologue of the neuroleptic agent octoclothepin with an eight-membered ring B. The present paper deals with experiments which partly preceded the just mentioned synthesis and according to the original project should be a model in a similar chlorine-free series. The unexpected results, however, led us to a completely different line of research.

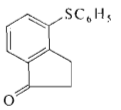
The starting topic was a study of cyclization of 3-[2-(phenylthio)phenyl]propionic acid (*I*) with polyphosphoric acid. The acid *I* was prepared by alkylation of diethyl malonate with 2-(phenylthio)benzyl chloride[2] and by the following hydrolysis of the ester *II* with 50% sulfuric acid at 165°C with simultaneous decarboxylation. We supposed that treatment with polyphosphoric acid will effect cyclization of the acid *I* to 4-(phenylthio)indanone (*III*) or 6,7-dihydrodibenzo[*b,g*]thiocin-5-one (*IV*), or a mixture of both. The formation of a five-membered ring was considered more

* Part CXXVIII in the series Neurotropic and Psychotropic Agents; Part CXXVII: This Journal *44*, 2108 (1979).

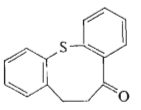
probable but the structure *III* requires an uneasy electrophilic attack to the *m*-position towards the phenylthio group. For this reason, the formation of *IV* could not be excluded. In a series of preliminary experiments, in which the reaction temperature was successively decreased starting from 150°C, there was established that a complete conversion of the acid *I* to neutral products takes place at 60–80°C already. Because of the fact that the reaction was accompanied with the formation of a dark-green colour, the lowest reaction temperature possible was considered optimum. Assuming a cleavage of one molecule of water from the acid *I*, the yield on the neutral product was a theoretical one.



I, $R^1 = H$, $R^2 = COOH$
II, $R^1 = R^2 = COOC_2H_5$

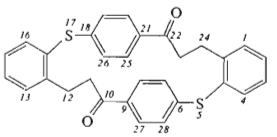


III



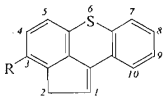
IV

Chromatography of this neutral product on a thin layer of alumina proved it to consist of three main components (A, B and C). Component A (6%) was separated on the basis of its very low solubility in benzene. It is a colourless solid $C_{30}H_{24}O_2S_2$ melting at 303–306°C. The IR spectrum showed an aryl ketone band at 1 680 cm^{-1} and the bands in the region of out-of-plane vibrations of the aromatic C—H bonds at 764 and 842 cm^{-1} indicated the presence of *o*- and *p*-substituted benzene nuclei. All of these facts led to formulating the product as the macrocyclic diketone *V*. A similar type of a "dimeric" macrocyclic diketone was obtained by Bickelhaupt and coworkers[3] in a reaction of 2-(2-phenylthioethyl)benzoic acid with polyphosphoric acid

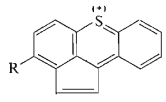


V

The benzene-soluble neutral product was chromatographed on a column of alumina giving 31% of the least polar component B, dark-green solid melting at 102 to 103°C, followed by a homogeneous oil (component C), obtained in a similar yield like component B. The analysis and the mass spectrum determined for component B the formula $C_{15}H_{10}S$; we are thus dealing here with a product of cleavage of two molecules of water from the starting acid *I*. The UV spectrum indicated a polycyclic conjugated system. In the IR spectrum, there are only two diagnostically valuable bands in the region of the out-of-plane vibrations of the aromatic C—H bonds at 750 and 761 cm^{-1}, corresponding to the presence of a 1,2-disubstituted and a 1,2,3-trisubstituted aromatic rings. This showed the presence of 7 aromatic protons which is in agreement with the ^{1}H-NMR spectrum, showing in addition a triplet at δ 6·39 ppm (J = 2·5 Hz), corresponding to one olefinic proton, and further a doublet at 3·40 ppm (J = 2·5 Hz), corresponding to two protons of a benzylic methylene group. All of these facts induced us to formulate the product B as 2*H*-cyclopenta[*kl*]thioxanthene (*VI*), derivative of a new tetracyclic system. The observed green colour hardly belongs to this compound; we suggest to explain it by the expected easy transformation of compound *VI* by the action of air oxygen to the thioxanthylium ion *VIII* for which the intensive colour would be very probable.



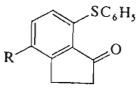
VI, R = H
VII, R = Cl



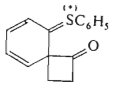
VIII, R = H
IX, R = Cl

Compound C has according to the mass spectrum and the analysis, the elemental composition $C_{15}H_{12}OS$. IR spectrum shows the carbonyl band at 1717 cm^{-1} which is a typical band of an indanone carbonyl group. UV and ^{1}H-NMR spectra are in agreement with the formulation of this compound as the indanone *III*. With respect to the parallel formation of compound *VI*, it was necessary to consider also the structure of the isomeric indanone *X*. The position of the carbonyl band in the IR spectrum of C, however, excludes structure *X*; due to the conjugation effect of the sulfur atom in *o*-position to the carbonyl group, this band must have been significantly shifted to lower frequencies. We are thus coming into a contradictious situation: on the one hand, indanone *III* is a logical product of cyclization of the acid *I*, on the other, one has to assume at least a transitional formation of the indanone *X* as the necessary precursor of the cyclopentathioxanthene *VI*. For the forma-

tion of compound *VI*, including a transitional formation of the indanone *X*, the following mechanism is being proposed: Cyclization of the primary acylium cation, corresponding to the acid *I*, into *m*-position towards the sulfur atom is evidently very difficult due to the tendency of the sulfur substituent to direct the course of an electrophilic substitution into *p*- or *o*-position. We assume, therefore, that the cyclization proceeds into the *o*-position and the primary product is a spirocyclic sulfonium cation *XII* which is stabilized by loosing a proton and rearrangement to the indanone *X*. This compound undergoes then in polyphosphoric acid quantitatively dehydrocyclization resulting in the cyclopentathioxanthene *VI*.

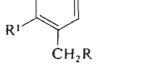


X, R = H
XI, R = Cl



XII

The hypothesis just described was preceded by another one in which we presumed that treatment of the acid *I* with polyphosphoric acid effects primarily a migration of the whole substituted alkyl group to the adjacent position of the aromatic ring, proceeding in a similar manner as the migration of alkyl groups on the aromatic ring under the influence of aluminium chloride, other Lewis acids or even sulfuric acid[4]. As the product (or one of the products) of this migration we thus assumed 3-[3-(phenylthio)phenyl]propionic acid (*XIIIa*), the cyclization of which could at least partly lead to the indanone *X*, necessary as precursor of formation of compound *VI*. For having an experimental evidence for supporting or refusing this hypothesis, we carried out the synthesis of the acid *XIIIa* and investigated its reaction with polyphosphoric acid.



a, $R^1 = H$
b, $R^1 = Cl$

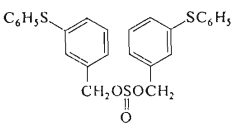
XIII, $R = CH_2COOH$
XIV, $R = OH$

XV, R = Cl
XVI, $R = CH(COOC_2H_5)_2$

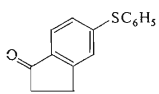
The known 3-(phenylthio)benzoic acid[5] was reduced with sodium dihydridobis-(2-methoxyethoxy)aluminate in benzene to the alcohol *XIVa* giving by treatment with

thionyl chloride in boiling benzene the substituted benzyl chloride *XVa*. In an attempt to react the alcohol *XIVa* with thionyl chloride in pyridine at room temperature, a stable sulfurous ester *XVII* was formed. Alkylation of diethyl malonate with the chloride *XVa* gave the malonic ester *XVIa*, which was transformed by alkaline hydrolysis to the corresponding malonic acid, decarboxylated in crude state by heating. There resulted the oily acid *XIIIa*.

The acid *XIIIa* was cyclized like the acid *I*, *i.e.* with polyphosphoric acid at 60 to 80°C. The neutral product, obtained in theoretical yield, was much less coloured than in the preceding case; it was chromatographed on alumina. Elution with benzene gave first 26% of less polar components in which thin layer chromatography detected clearly the presence of the cyclopentathioxanthene *VI*. It did not succeed in this case to isolate this product in crystalline state neither by inocculation with the pure compound, nor by rechromatography of the whole fraction. In a small extent, the expected cyclization to the indanone *X* and its following dehydrocyclization took evidently place but decidedly in a much lesser degree than in the case of cyclization of the acid *I*. Continuation of the chromatography yielded 21% of a more polar crystalline phenylthioindanone $C_{15}H_{12}OS$. The carbonyl band in its IR spectrum is shifted to 1693 cm^{-1}. The structure *XVIII* was assigned to this product which is in agreement with the spectra recorded and with the conjugation effect of the sulfur atom in *p*-position towards carbonyl group of the indanone ring. No further homogeneous substance could be isolated from the cyclization of the acid *XIIIa* and some 40% of the material could not be washed out from the column of alumina. In conclusion, this experiment did not support our hypothesis on a migration of the whole carboxyalkyl residue in the acid *I* when exposed to polyphosphoric acid; this hypothesis was evidently wrong.



XVII

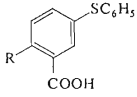


XVIII

In connection with the investigations described, we carried out an additional experiment, in which the *p*-position towards the sulfur atom in the acid *XIIIa* was blocked, the cyclization to the *p*-position was consequently eliminated, on the other hand the cyclization to the *o*-position became unequivocal and in this way the possibility of formation of a cyclopentathioxanthene derivative should be increased.

Atom of chlorine was used for blocking the said *p*-position and the substrate for cyclization was thus 3-[2-chloro-5-(phenylthio)phenyl]propionic acid (*XIIIb*).

The synthesis of the acid *XIIIb* was carried out by a seven-step synthesis starting from 5-chloro-2-nitrobenzoic acid. Its reaction with thiophenol in a boiling aqueous solution of potassium hydroxide in the presence of copper gave the nitro acid *XIX* which was reduced with hydrazine to the amino acid *XX*. The preparation of this compound by a different method has already been described in a patent[6]. The following Sandmeyer reaction afforded the chloro acid *XXI*. Reduction of the acid *XXI* with sodium dihydridobis(2-methoxyethoxy)aluminate resulted in the alcohol *XIVb* which was transformed with thionyl chloride to the chloride *XVb*. This was used to alkylate diethyl malonate and the obtained malonic ester *XVIb* was subjected to alkaline hydrolysis; the corresponding malonic acid formed was thermically decarboxylated in crude state to the required acid *XIIIb*.



XIX, R = NO_2
XX, R = NH_2
XXI, R = Cl

The acid *XIIIb* was cyclized with polyphosphoric acid at 120–140°C (15 hours). If we consider the cleavage of 1–2 molecules of water, the yield on the neutral product is theoretical. This neutral product was dark-green, inhomogeneous, but crystalline. On the basis of low solubility in ethanol, 7% of a colourless solid (substance D), melting at 224–225°C, were separated. Processing of the filtrate by a combination of crystallization and chromatography led to the isolation of substance E, crystallizing in green prisms and melting at 114–115°C. This substance is the main reaction product, being formed in a yield of 50%. Rechromatography of the mother liquors led to the isolation of an additional crystalline compound (substance F), melting at 122–123°C and being obtained in a yield of 5%. A direct comparison of compounds E and F excluded their identity. If the reaction time was prolonged to 20 hours and the neutral product was directly processed by chromatography, substance E was the only isolated product in a yield of 85%. The mass spectrum and analysis settled the empirical composition to be $C_{15}H_9ClS$ and the other spectra determined for it unequivocally the structure of the expected 3-chloro-2*H*-cyclopenta[*kl*]thioxanthene (*VII*). A comparison of these spectra with those of the non-chlorinated compound *VI* represents a confirmation of structure *VI* and of the correctness of our argumentation in connection with the course of cyclization of the acid *I*. When heated and contacted with air, compound *VII* turns very dark-green (almost black) which is ascribed to the formation of the thioxanthylium cation *IX*. An attempt to carry out preparati-

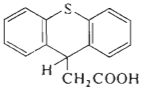
vely the oxidation of compound *VII* with mercuric acetate in the presence of perchloric acid did not lead to a characterized product. Likewise without success was an attempt to transform compound *VII* to compound *VI* by hydrogenolysis with sodium dihydridobis(2-methoxyethoxy)aluminate in the presence of bis(benzylcyano)palladium chloride (for the method, *cf.*[7]). In both cases the products were almost black substances melting around 300°C. The highly conjugated system of compounds *VI* and *VII* is evidently the cause of their tendency to polymerization reactions.

Substance D, having a high melting point, corresponds analytically very well to a dimer of compound *VII*. Determination of the molecular ion by measurement of the mass spectrum, proved, however, difficult. Molecular peaks at *m/e* 508 and 510 indicate rather a composition of a dimer of compound *VII* less 2 H, and 4 H, respectively. The base peak has *m/e* 255; another abundant fragment of *m/e* 221 occurs also in the spectrum of compound *VII*. The UV spectrum of substance D is very similar to that of compound *VII*. A normal recording of the ^{1}H-NMR spectrum was not possible because of the insolubility in the solvents used. It was possible, however, to prepare solution of substance D in hot pentadeuteropyridine and octadeuterodioxane. However, during preparation of these solutions, chemical transformations took place, manifested by the intensive colour of the solutions.

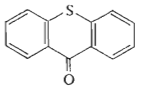
Substance F was identified as the indanone *XI*. On the basis of the conjugation effect of the sulfur atom in *o*-position towards the carbonyl group of the indanone ring, it shows again an anomalously shifted carbonyl band in the IR spectrum to lower frequencies: 1694 cm^{-1}. This compound is the intermediate in the transformation of the acid *XIIIb* to compound *VII*. The occurrence of only a small amount of *XI* in the reaction mixture indicates that the dehydrocyclization reaction proceeds smoothly under the conditions used.

The unexpected formation of 2*H*-cyclopenta[*kl*]thioxanthene derivatives induced us to carry out another experiment. According to the literature[8], thioxanthene-9-acetic acid (*XXII*) has been synthesized and we attempted its cyclization with polyphosphoric acid at 120–140°C. No cyclization into the *m*-position towards the sulfur atom could be detected. Instead of that, a completely different escaping reaction took place: thioxanthone (*XXIII*) and thioxanthene (*XXIV*) were isolated as the main products. A cleavage of acetic acid molecule took place and the thioxanthylium cation was formed; the disproportionation of thioxanthylium salts on hydrolysis to thioxanthones and thioxanthenes was described[9]. As a minor product, a compound $C_{26}H_{18}OS_2$ was isolated, melting at 175–179°C. This composition corresponds to 9,9'-dithioxanthyl ether (*XXV*) which could be a product of interaction of the thioxanthylium cation with thioxanthydrol but for which a m.p. of 314–316°C was reported[10]. A recent paper[11] describes the ether *XXV* as a compound melting at 189–190°C which makes the identity of the high-melting substance[10] doubtful. We ascribed thus to our minor product the structure of the ether *XXV* and the lower

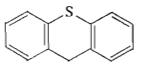
melting point has to be explained by the presence of a small amount of thioxanthone as an impurity (proven by the mass spectrum).



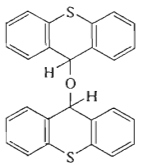
XXII



XXIII



XXIV



XXV

EXPERIMENTAL

The melting points of the analytical preparations were determined in an automatic Mettler FP-5 melting point recorder. The samples were dried at about 70 Pa over P_2O_5 at room temperature or at 77°C. UV spectra (in methanol) were registered with a Unicam SP 8000 spectrophotometer, IR spectra (in Nujol unless stated otherwise) with a Unicam SP 200G spectrophotometer, ^{1}H-NMR spectra (in $CDCl_3$ unless stated otherwise) were produced with a Tesla BS 487C (80 MHz) spectrometer, and the mass spectra were recorded with a MS 902 (AEI) or a Varian MAT 311 spectrometers. The homogeneity of the compounds was checked by thin-layer chromatography on silica gel (Silufol) or alumina.

2-Nitro-5-(phenylthio)benzoic Acid (*XIX*)

Thiophenol (38·5 g) was dissolved in a solution of 66 g KOH in 700 ml water, the solution was treated with 70·3 g 5-chloro-2-nitrobenzoic acid and 4·0 g "molecular" copper, and the mixture was refluxed for 7 h under stirring in an atmosphere of nitrogen. After standing overnight, the mixture was filtered and the filtrate acidified with hydrochloric acid. After standing for another 24 h, the separated product was filtered, washed with water, dried *in vacuo* and dissolved in 200 ml chloroform. The solution was filtered and chromatographed on a column of 250 g silica gel. Chloroform eluted 91·2 g product which was crystallized from a mixture of benzene and light petroleum; 79 g (82%), m.p. 127—129°C. Analytical sample (yellowish prisms), m.p. 131—132°C (benzene). UV spectrum: λ_{max} 210 nm (log ε 4·42), infl. 250 nm (3·92), 335 nm (3·99). IR spectrum: 686, 703, 750, 830, 878 (5 and 2 adjacent and solitary Ar—H), 920, 1267, 1288 (COOH), 1362, 1527 ($ArNO_2$), 1700 (ArCOOH), 2520, 2645, 3100 cm^{-1} (COOH). ^{1}H-NMR spectrum:

δ 11·95 (s, 1 H, COOH), 7·80 (d, J = 8·5 Hz, 1 H, 3-H), 7·35—7·70 (m, 5 H, C_6H_5), 7·45 (mcs, J = 2·0 Hz, 1 H, 6-H), 7·25 (mcd, J = 8·5; 2·0 Hz, 1 H, 4-H). For $C_{13}H_9NO_4S$ (275·3) calculated: 56·72% C, 3·29% H, 5·09% N, 11·65% S; found: 56·98% C, 3·31% H, 4·90% N, 11·39% S.

2-Amino-5-(phenylthio)benzoic Acid (*XX*)

A solution of 93 g *XIX* in 650 ml ethanol, prepared at 45°C, was stirred and treated with 14 g, charcoal, 44·6 g 80% hydrazine hydrate and a solution of 2·8 g $FeCl_3.6\,H_2O$ in 65 ml ethanol. The mixture was stirred for 40 min at 45°C and then carefully warmed by a water bath. At 60°C, an exothermic reaction took place and the bath was removed. After cessation of the spontaneous reaction, the mixture was refluxed for 10 h, filtered while hot and the filtrate evaporated *in vacuo*. The residue was mixed with 400 ml cold water, 12 ml acetic acid were added, the solid was filtered, washed with water and dried *in vacuo*; 75·4 g (92%), m.p. 209—211°C. Analytical sample was obtained by crystallization from ethanol, m.p. 213—214°C. A patent[6] describing the synthesis of this compound by a completely different method, reported a m.p. of 211—212°C without any analytical or spectral characterization. UV spectrum: λ_{max} 222 nm (log ε 4·50), 267·5 nm (4·28), 341 nm (3·61). IR spectrum: 690, 705, 738, 820, 895 (5 and 2 adjacent and solitary Ar—H), 910, 1242, 1680, 2610, 2700 (COOH), 1479, 1547, 1580 (Ar), 1606, 3340, 3462 cm^{-1} (NH_2). ^{1}H-NMR spectrum (CD_3SOCD_3): δ 8·20—9·50 (COOH, NH_2 and H_2O from the solvent), 7·90 (mcs, J = 2·5 Hz, 1 H, 6-H), 7·35 (mcd, J = 8·0; 2·5 Hz, 1 H, 4-H), 7·00—7·40 (m, 5 H, C_6H_5), 6·88 (d, J = 8·0 Hz, 1 H, 3-H). For $C_{13}H_{11}NO_2S$ (245·3) calculated: 63·65% C, 4·52% H, 5·71% N, 13·07% S; found: 63·01% C, 4·63% H, 5·47% N, 13·26% S.

2-Chloro-5-(phenylthio)benzoic Acid (*XXI*)

XX (78·9 g) was dissolved in a solution of 16 g NaOH in 400 ml water, 28 g $NaNO_2$ were added and the solution filtered. The filtrate was then added dropwise over 1 h to a stirred solution of 65 g Cu_2Cl_2 in 320 ml hydrochloric acid at 0—2°C. The separated product was extracted with hot benzene, the extract was evaporated and the residue crystallized from benzene giving the first crop of crystals. The second one was obtained by chromatography of the mother liquors on a column of 250 g silica gel and elution with benzene; the total yield was 56·3 g (66%), m.p. 107—109°C. Analytical sample, m.p. 109—110°C (cyclohexane). UV spectrum: λ_{max} 256·5 nm (log ε 4·11), infl. 277 nm (3·92). IR spectrum: 688, 732, 744, 818, 898 (5 and 2 adjacent and solitary Ar—H), 1250, 1692, 2465, 2513, 2615, 2700, 2860, 3120 (COOH), 1472, 1552, 1579, 3040, 3060 cm^{-1} (Ar). ^{1}H-NMR spectrum: δ 12·08 (bs, 1 H, COOH), 7·90 (mcs, 1 H, 6-H), 7·32 (m, 7 H, remaining Ar—H). For $C_{13}H_9ClO_2S$ (264·7) calculated: 58·98% C, 3·43% H, 13·39% Cl, 12·11% S; found: 59·01% C, 3·19% H, 13·23% Cl, 11·97% S.

3-(Phenylthio)benzyl Alcohol (*XIVa*)

A stirred suspension of 13·8 g 3-(phenylthio)benzoic acid[5] in 135 ml benzene was treated dropwise over 1 h with 40 ml 50% sodium dihydridobis(2-methoxyethoxy)aluminate in benzene (temperature rose spontaneously to 40—50°C). The mixture was stirred for 3 h at room temperature and under cooling, it was decomposed by a slow addition of 75 ml 10% NaOH. After 1 h stirring, the benzene layer was separated, dried with K_2CO_3 and evaporated under reduced pressure. The residue was distilled; 10·2 g (79%), b.p. 130—132°C/33 Pa. A redistilled sample (b.p. 127—128°C/13 Pa) was analyzed. Mass spectrum, *m/e* (%): 216 (M^+, 100), 199 (15), 185 (51), 109 (33), 77 (46). IR spectrum (film): 699, 748, 792 (Ar—H), 1030 (CH_2OH), 1479, 1573, 1585, 1596, 3060 (Ar), 3340 cm^{-1} (OH). ^{1}H-NMR spectrum: δ 7·20 (m, 9 H, Ar—H), 4·50 (d, J =

= 6·0 Hz, after D_2O s, 2 H, $ArCH_2O$), 2·25 (t, J = 6·0 Hz, disappears after D_2O, 1 H, OH). For $C_{13}H_{12}OS$ (216·3) calculated: 72·19% C, 5·59% H, 14·82% S; found: 72·04% C, 5·56% H, 15·00% S.

2-Chloro-5-(phenylthio)benzyl Alcohol (*XIVb*)

XXI (41 g) in 200 ml benzene was reduced with 170 ml 50% sodium dihydridobis(2-methoxyethoxy)aluminate like in the preceding case; 32·5 g (84%), b.p. 154—156°C/26 Pa. ^{1}H-NMR spectrum: δ 7·00—7·50 (m, 8 H, Ar—H), 4·60 (s, 2 H, $ArCH_2O$), 2·18 (bs, 1 H, OH). For $C_{13}H_{11}$·.ClOS (250·7) calculated: 62·27% C, 4·42% H, 14·14% Cl, 12·79% S; found: 62·32% C, 4·43% H, 13·91% Cl, 12·72% S.

3-(Phenylthio)benzyl Chloride (*XVa*)

A refluxing solution of 8·65 g *XIVa* in 40 ml benzene was stirred and treated dropwise with 7·2 g $SOCl_2$ over 45 min. After 15 min of refluxing, volatile components were evaporated under reduced pressure. The residue was distilled; 8·8 g (94%), b.p. 107—108°C/13 Pa. ^{1}H-NMR spectrum: δ 7·25 (m, 9 H, Ar—H), 4·49 (s, 2 H, $ArCH_2$). For $C_{13}H_{11}ClS$ (234·7) calculated: 66·52% C, 4·72% H, 15·10% Cl, 13·66% S; found: 66·91% C, 4·91% H, 15·41% Cl, 13·98% S.

Bis[3-(phenylthio)benzyl] Sulfite (*XVII*)

A mixture of 17·0 g *XIVa* and 6·5 ml pyridine was stirred and treated over 40 min with 9·4 g $SOCl_2$ at 10—20°C. After standing for 3 h at room temperature, the mixture was diluted with 200 ml chloroform, the solution was washed with water and 10% Na_2CO_3 solution, dried with $MgSO_4$ and evaporated. The residue (16·5 g, 88%) melted at 57—59°C. Analytical sample, m.p. 61°C (ether–light petroleum). Mass spectrum, *m/e*: 478·072 (M^+ corresponding to $C_{26}H_{22}O_3S_3$). ^{1}H-NMR spectrum: δ 7·00—7·40 (m, 18 H, Ar—H), 4·92 and 4·70 (ABq, J = = 12·0 Hz, 4 H, 2 $ArCH_2O$). For $C_{26}H_{22}O_3S_3$ (478·6) calculated: 65·24% C, 4·63% H, 20·10% S; found: 65·58% C, 4·77% H, 20·06% S.

2-Chloro-5-(phenylthio)benzyl Chloride (*XVb*)

A solution of 15·0 g *XIVb* in 45 ml benzene was added dropwise to a stirred refluxing mixture of 15 g $SOCl_2$, 45 ml benzene and 3 ml pyridine over 30 min. The mixture was refluxed for 1 h, cooled, decomposed with 100 ml water, the benzene layer was washed with water, 5% NaOH and water, dried ($CaCl_2$) and evaporated. The residue (15·5 g, 94%) is almost homogeneous and was used directly for further work. A sample was distilled for analysis, b.p. 132—133°C/20 Pa (partial decomposition). ^{1}H-NMR spectrum: δ 7·38 (mcs, J = 2·0 Hz, 1 H, 6-H), 7·30 (s, 5 H, C_6H_5), 7·28 (d, J = 8·0 Hz, 1 H, 3-H), 7·10 (mcd, J = 8·0; 2·0 Hz, 1 H, 4-H), 4·58 (s, 2 H, $ArCH_2Cl$). For $C_{13}H_{10}Cl_2S$ (269·2) calculated: 58·00% C, 3·74% H, 26·34% Cl, 11·91% S; found: 59·05% C, 3·91% H, 25·70% Cl, 12·20% S.

Diethyl 2-(Phenylthio)benzylmalonate (*II*)

A solution of sodium ethoxide (115 ml ethanol, 5·15 g Na) was treated with 35·7 g diethyl malonate and the solution stirred for 15 min. It was then treated dropwise over 1 h with 52·2 g 2-(phenylthio)benzyl chloride[2] at 60—70°C under stirring and the mixture was refluxed for 12 h. Ethanol was evaporated *in vacuo*, the residue was decomposed with water and extracted with benzene.

The extract was dried with $MgSO_4$ and distilled; 38·0 g (48%), b.p. 186—192°C/67 Pa. For analysis, the product was redistilled, b.p. 188—193°C/67 Pa. For $C_{20}H_{22}O_4S$ (358·4) calculated: 67·02% C, 6·19% H, 8·93% S; found: 67·26% C, 6·23% H, 9·25% S.

Diethyl 3-(Phenylthio)benzylmalonate (*XVIa*)

Diethyl malonate (14·1 g) was reacted with sodium ethoxide (from 50 ml ethanol and 2·05 g Na), the solution treated with 20·7 g *XVa* and the mixture processed like in the preceding case; 27·8 g (88%) crude product which was used for the hydrolysis. A sample was distilled for analysis, b.p. 152—153°C/13 Pa. ^{1}H-NMR spectrum: δ 7·00—7·40 (m, 9 H, Ar—H), 4·12 (q, 4 H, 2 OCH_2), 3·60 (t, 1 H, COCHCO), 3·12 (d, 2 H, $ArCH_2$), 1·18 (t, 6 H, 2 CH_3). For $C_{20}H_{22}O_4S$ (358·4) calculated: 67·01% C, 6·19% H, 8·94% S; found: 66·91% C, 6·21% H, 9·16% S.

Diethyl 2-Chloro-5-(phenylthio)benzylmalonate (*XVIb*)

Was prepared like in the foregoing cases from 12·8 g diethyl malonate, 70 ml ethanol, 1·85 g Na and 18·5 g *XVb*; 26·2 g (97%) crude product which was used for further work. A sample was distilled for analysis, b.p. 190°C/20 Pa. IR spectrum (film): 692, 744, 820, 860 (5 and 2 adjacent and solitary Ar—H), 1 049, 1 157, 1 230, 1 745 (R—COOH), 1 585, 3 045, 3 060 cm^{-1} (Ar). ^{1}H-NMR spectrum: δ 7·00—7·30 (m, 8 H, Ar—H), 4·08 (q, J = 7·0 Hz, 4 H, 2 OCH_2), 3·71 (t, J = = 8·0 Hz, 1 H, COCHCO), 3·20 (d, J = 8·0 Hz, 2 H, $ArCH_2$), 1·11 (t, J = 7·0 Hz, 6 H, 2 CH_3). For $C_{20}H_{21}ClO_4S$ (392·9) calculated: 61·14% C, 5·39% H, 9·02% Cl, 8·16% S; found: 61·62% C, 5·68% H, 8·80% Cl, 8·48% S.

3-[2-(Phenylthio)phenyl]propionic Acid (*I*)

A mixture of 35·5 g *II* and 135 ml 50% H_2SO_4 was stirred and heated for 13 h to 165°C. After cooling, it was diluted with 250 ml water and the product was extracted with benzene. The acidic product was transferred by shaking with an excess of 10% NaOH into the aqueous phase, the alkaline solution was separated and acidified with hydrochloric acid. The product separated in a yield of 17·7 g (69%), m.p. 89—93°C. The pure acid was obtained by crystallization from 80% aqueous ethanol, m.p. 97—99°C. For $C_{15}H_{14}O_2S$ (258·3) calculated: 69·75% C, 5·46% H, 12·41% S; found: 70·07% C, 5·61% H, 12·48% S.

3-[3-(Phenylthio)phenyl]propionic Acid (*XIIIa*)

A mixture of 10·0 g crude *XVIa* and 100 ml 20% NaOH was stirred and refluxed for 13 h (bath temperature 140—145°C). After cooling, the mixture was diluted with water, acidified with hydrochloric acid and extracted with benzene. The extract was shaken with an excess of 10% NaOH. The alkaline solution and the oily sodium salt were combined and acidified with hydrochloric acid. The separated malonic acid was isolated by extraction with chloroform, the extract was dried with $CaCl_2$ and evaporated. The residue (7·5 g) was heated for 1 h to 160—170°C with evolution of CO_2. The remaining oil (6·2 g, 86%) is the crude acid *XIIIa*, a sample of which was distilled for analysis, b.p. 182—186°C/13 Pa. IR spectrum (film): 695, 746, 795, 877, 891 (5 and 3 adjacent and solitary Ar—H), 950, 1 220, 1 249, 1 291, 1 710, 2 660, 3 400 (COOH), 1 480, 1 574, 1 583, 1 594, 3 055 cm^{-1} (Ar). ^{1}H-NMR spectrum: δ 11·18 (bs, 1 H, COOH), 6·90—7·40 (m, 9 H, Ar—H), 2·40—3·00 (m, 4 H, $ArCH_2CH_2CO$). For $C_{15}H_{14}O_2S$ (258·3) calculated: 69·74% C, 5·46% H, 12·41% S; found: 70·01% C, 5·64% H, 12·40% S.

3-[2-Chloro-5-(phenylthio)phenyl]propionic Acid (*XIIIb*)

Crude *XVIb* (26·2 g) was refluxed for 8 h with a solution of 40 g KOH in 200 ml ethanol. After standing overnight, the separated potassium salt was filtered with suction, dissolved in 100 ml water, the solution acidified with hydrochloric acid and the separated malonic acid extracted with benzene. Evaporation of the extract gave 12·5 g residue which was decarboxylated by heating for 1 h to 160—170°C; 10·1 g (52%) crude *XIIIb*. For purification, this product was first distilled (b.p. 190—200°C/33 Pa) and then crystallized from cyclohexane, m.p. 81—82°C. IR spectrum: 692, 751, 812, 875 (5 and 2 adjacent and solitary Ar—H), 930, 1217, 1310, 1709, 2550, 2645, 2700, 3100 (COOH), 1480, 1585 cm^{-1} (Ar). ^{1}H-NMR spectrum: δ 11·38 (bs, 1 H, COOH), 6·90—7·40 (m, 8 H, Ar—H), 2·50—3·10 (m, 4 H, $ArCH_2CH_2CO$). For $C_{15}H_{13}ClO_2S$ (292·8) calculated: 61·54% C, 4·47% H, 12·11% Cl, 10·95% S; found: 62·07% C, 4·62% H, 12·35% Cl, 11·24% S.

2*H*-Cyclopenta[*k,l*]thioxanthene (*VI*)

A mixture of 6·0 g I and 200 g polyphosphoric acid was stirred for 30 h at 60—80°C. After cooling, the mixture was decomposed with 1 l water and extracted with benzene. The dark-green extract was washed with 10% NaOH, dried with K_2CO_3 and evaporated. The residue (5·6 g) was dissolved in 15 ml benzene and the solution allowed to stand overnight. There separated 0·36 g (6%) of a colourless substance A which was recrystallized from toluene and melted at 303 to 306°C. On the basis of the following data, it was identified as 11,12,23,24-tetrahydro-6,9;18,21-diethenodibenzo[*b,l*]-1,11-dithiacycloeicosin-10,22-dione (*V*). Mass spectrum, *m/e* (%): 480 (M^+, 100), 462 (2, M—H_2O), 452 (4, M—CO), 451 (4), 447 (5), 343 (23), 328 (8), 316 (6), 253 (30), 239 (76), 211 (24), 207 (47), 197 (59), 135 (44). UV spectrum (saturated solution): λ_{max} 299 nm. IR spectrum: 764, 781, 799, 842 (4 and 2 adjacent Ar—H), 978, 1090, 1189, 1213, 1561, 1590 (Ar), 1680 cm^{-1} (Ar—CO). For $C_{30}H_{24}O_2S_2$ (480·5) calculated: 74·99% C, 5·03% H, 13·32% S; found: 74·99% C, 5·10% H, 13·06% S.

The benzene mother liquor was evaporated and the green amorphous residue (5·2 g) was chromatographed on a column of 250 g neutral alumina (activity II). Benzene eluted first 1·6 g (31%) of the substance B which was crystallized from a mixture of ethanol and benzene; greenish prisms, m.p. 102—103°C. It was identified by spectra and analysis to be *VI*. Mass spectrum, *m/e* (%): 222 (M^+, 100, corresponding to $C_{15}H_{10}S$), 221 (100, M—H), 219 (20), 189 (22), 176 (21), 151 (8), 150 (9), 111 (39), 97 (11), 88 (15). UV spectrum: λ_{max} 230 nm (log ε 4·61), infl. 235 nm (4·55), 251 nm (4·20), 259 nm (4·18), 273 nm (4·20), 353 nm (3·55), 369 nm (3·51). IR spectrum: 750, 761 (4 and 3 adjacent Ar—H), 978, 1040, 1069, 1110, 1185, 1551, 1567, 1609 cm^{-1} (Ar). ^{1}H-NMR spectrum: δ 7·59 (m, 1 H, 10-H), *c.* 7·00 (m, 6 H, remaining Ar—H), 6·39 (t, J = 2·5 Hz, 1 H, 1-H), 3·40 (d, J = 2·5 Hz, 2 H, $ArCH_2$). For $C_{15}H_{10}S$ (222·2) calculated: 81·06% C, 4·54% H, 14·40% S; found: 81·15% C, 4·79% H, 14·23% S.

Continuation of the chromatography with elution with benzene gave 1·8 g (32%) of the oily substance C, identified to be 4-(phenylthio)indanone (*III*). For analysis, it was distilled, b.p. 180—190°C/20 Pa. Mass spectrum, *m/e*: 240 (M^+, corresponding to $C_{15}H_{12}OS$), 212, 178, 134. UV spectrum: λ_{max} 241·5 nm (log ε 4·44), infl. 260 nm (4·05), 317 nm (3·43). IR spectrum (film): 694, 750, 775 (5 and 3 adjacent Ar—H), 1262, 1429 (ArCOR), 1588, 3065 (Ar), 1717 cm^{-1} (Ar—CO in a 5-membered ring). ^{1}H-NMR spectrum: δ 7·00—7·70 (m, 8 H, Ar—H), 3·00 (m, 2 H, $ArCH_2$), 2·65 (m, 2 H, $COCH_2$). For $C_{15}H_{12}OS$ (240·3) calculated: 74·97% C, 5·03% H, 13·34% S; found: 75·12% C, 5·25% H, 13·55% S.

5-(Phenylthio)indanone (*XVIII*)

A mixture of 6·0 g *XIIIa* and 200 g polyphosphoric acid was stirred for 30 h at 60—80°C and processed like in the preceding case and gave 5·80 g neutral oily product. This was chromatographed on a column of 250 g neutral alumina (activity II). Elution with benzene gave first 1·35 g of the least polar oily components where the presence of *VI* was detected by TLC. An attempt to isolate this substance by rechromatography on Al_2O_3 was not successful.

Continuation of the chromatography using benzene still as the eluent gave 1·17 g (21%) of a crystalline fraction, m.p. 60—61°C (benzene–light petroleum), identified to be *XVIII*. UV spectrum: λ_{max} 242 nm (log ε 4·08), infl. 255 nm (3·83), infl. 292 nm (4·08), 313 nm (4·29). IR spectrum (KBr): 690, 709, 752, 819, 835, 874 (5 and 2 adjacent and solitary Ar—H), 1 590, 3048 (Ar), 1 693 cm^{-1} (ArCO in a 5-membered ring with a p-standing SAr). ^{1}H-NMR spectrum: δ 6·90 to 7·80 (m, 8 H, Ar—H), 3·00 (m, 2 H, $ArCH_2$), 2·60 (m, 2 H, $COCH_2$). For $C_{15}H_{12}OS$ (240·3) calculated: 74·97% C, 5·03% H, 13·34% S; found: 75·25% C, 5·15% H, 13·04% S.

3-Chloro-2*H*-cyclopenta[*k,l*]thioxanthene (*VII*)

A mixture of 5·0 g *XIIIb* and 100 g polyphosphoric acid was stirred and heated for 15 h to 120 to 140°C. Processing like in the preceding cases gave 4·1 g dark crystalline (inhomogeneous) neutral product. It was dissolved in 100 ml boiling ethanol and the insoluble colourless solid (substance D) was filtered off; 0·30 g (7%), m.p. 224—225°C (benzene). Mass spectrum (210°C), *m/e* (%): 510 (M^+?, 4·5, corresponding to $C_{30}H_{16}Cl_2S_2$), 508 (M^+?, 5, corresponding to $C_{30}.H_{14}Cl_2S_2$), 472 (1, 508—HCl), 438 (3, 508—Cl_2), 404 (0·3), 256 (30), 255 (100), 236 (4), 221 (35, 256—Cl), 219 (20, 255—HCl), 210 (1), 194 (2), 187 (4), 176 (10, 255—HCl—HS), 150 (3), 88 (8), 78 (6). UV spectrum (saturated solution): λ_{max} 234, 256, 265, 277, 360, 378 nm. IR spectrum: 750, 800 (Ar—H), 1 556, 1 610, 3 045 cm^{-1} (Ar). ^{1}H-NMR spectrum (C_5D_5N): δ 6·80—7·50 (m, 12 H, Ar—H), 6·30 (s, 2 H, 2C=CH), 5·30 (s, 2 H, C=CH_2). ^{1}H-NMR spectrum ($C_4D_8O_2$): δ 6·85 to 7·70 (m, 12 H, Ar—H), 6·00 (bs, 2 H, 2 C=CH), 5·20 (bs, 2 H, C=CH_2). For $C_{30}H_{16}Cl_2S_2$ (509·5) and $C_{30}H_{14}Cl_2S_2$ (507·5) calculated: 70·72 and 71·01% C, 3·17 and 2·78% H, 13·92 and 13·97% Cl, 12·19 and 12·24% S; found: 70·20% C, 3·13% H, 13·88% Cl, 12·12% S.

The ethanol mother liquor was evaporated and the residue recrystallized from a mixture of benzene and cyclohexane; 2·20 g (50%) crude substance E, m.p. 106—111°C. For analysis, the substance was purified by chromatography on a column of 40 g neutral Al_2O_3 (activity II) and by crystallization of the benzene eluate from a mixture of ethanol and benzene, m.p. 114—115°C. The following data identified substance E to be *VII*. Mass spectrum, *m/e* (%): 256 (M^+, 55, corresponding to $C_{15}H_9ClS$), 221 (100, M—Cl), 176 (10), 150 (4), 128 (7), 111 (23), 88 (18). UV spectrum (heptane): λ_{max} 234·5 nm (log ε 4·73), 255·7 nm (4·26), 264 nm (4·32), 276·7 nm (4·33), 299 nm (3·45), 311·5 nm (3·53), 341·5 nm (3·47), 356 nm (3·64), 374 nm (3·71). IR spectrum (CS_2): 736, 748, 799 (4 and 2 adjacent Ar—H), 850 (R_2C=CHR), 3 045 cm^{-1} (Ar). ^{1}H-NMR spectrum: δ 7·60 (m, 1 H, 10-H), *c* 7·12 (m, 3 H, 7,8,9-H_3), 7·03 and 6·87 (ABq, J = 8·5 Hz, 2 H, 4,5-H_2), 6·45 (t, J = 2·3 Hz, 1 H, 1-H), 3·44 (d, J = 2·3 Hz, 2 H, $ArCH_2$). For $C_{15}H_9ClS$ (256·7) calculated: 70·17% C, 3·53% H, 13·81% Cl, 12·49% S; found: 69·98% C, 3·59% H, 13·76% Cl, 12·68% S.

All mother liquors were combined and evaporated *in vacuo*. The residue (2·6 g) was rechromatographed on a column of 100 g neutral Al_2O_3 (act.II). After having eluted with benzene 1·38 g of the least polar components (consisting mainly of *VII*), a somewhat more polar crystalline fraction (0·25 g, 5%, substance F) was obtained (continued elution with benzene), m.p. 118 to 122°C. Analytical sample, m.p. 122—123°C (benzene–ethanol). The substance was identified as 4-chloro-7-(phenylthio)indanone (*XI*). UV spectrum: λ_{max} 214 nm (log ε 4·34), 233·5 nm

(4·34), 239·5 nm (4·34), 266 nm (3·88), 275 nm (3·94), 341 nm (3·83). IR spectrum (KBr): 700, 710, 760, 812 (5 and 2 adjacent Ar—H), 1480, 1570, 3040, 3060 (Ar), 1694 cm^{-1} (Ar—CO in a 5-membered ring with an *o*-standing SAr). ^{1}H-NMR spectrum: δ 7·50 (m, 5 H, C_6H_5), 7·25 (d, J = 8·0 Hz, 1 H, 5-H), 6·52 (d, J = 8·0 Hz, 1 H, 6-H), 3·12 (m, 2 H, $ArCH_2$), 2·85 (m, 2 H, $COCH_2$). For $C_{15}H_{11}ClOS$ (274·8) calculated: 65·57% C, 4·03% H, 12·90% Cl, 11·67% S; found: 66·02% C, 4·02% H, 13·06% Cl, 11·84% S.

In another experiment, carried out at 110—120°C for 20 h, the neutral product (4·1 g obtained from 4·7 g *XIIIb*) was directly chromatographed on 100 g Al_2O_3. Substance D and F were not isolated at all and the main chromatographic fraction (3·50 g, 85%), eluted with benzene, was the substance E (*VII*).

Reaction of Thioxanthene-9-acetic Acid (*XXII*) with Polyphosphoric Acid

Thioxanthene-9-acetic acid (*XXII*) was prepared by heating thioxanthene-9-ol[12] with malonic acid in pyridine (ref.[8]) in a yield of 87%, m.p. 170—171·5° (50% aqueous ethanol). The literature[8] reported a m.p. of 167—168°C. IR spectrum: 746, 764 (4 adjacent Ar—H), 946, 1291, 1304, 1705, infl. 3150 cm^{-1} (COOH). ^{1}H-NMR spectrum (CD_3SOCD_3): δ 7·10—7·60 (m, 8 H, Ar—H), 4·59 (t, J = 7·0 Hz, 1 H, Ar_2CH), 2·61 (d, J = 7·0 Hz, 2 H, CH_2CO). For $C_{15}H_{12}O_2S$ (256·3) calculated: 70·29% C, 4·72% H, 12·51% S; found: 70·59% C, 4·94% H, 12·47% S.

A mixture of 5·0 g *XXII* and 100 g polyphosphoric acid was stirred and heated to 120—140°C for 15 h (odor of acetic acid). The mixture was decomposed with 1 kg water, the solid filtered, washed with water, suspended into 200 ml 5% NaOH and extracted with 200 ml boiling benzene. The undissolved substance was filtered off (0·6 g, m.p. over 290°C) and the benzene layer of the filtrate was evaporated. The dark residue (3·5 g) was crystallized from benzene to give 0·90 g thioxanthone (*XXIII*), m.p. 214—215°C, identified by analysis and by comparison with the authentic product, m.p. 209°C (ref.[13]).

The mother liquor was evaporated, the residue dissolved in benzene and the solution chromatographed on a column of 100 g neutral alumina (act. II). Benzene eluted 2·22 g inhomogeneous crystalline solid which was extracted with 25 ml boiling light petroleum. The undissolved fraction was filtered off and the filtrate allowed to crystallize on standing; 0·45 g thioxanthene (*XXIV*), m.p. 124—128°C, identified by analysis and by comparison with the authentic product, m.p. 128°C (ref.[14]).

The fraction which was insoluble in light petroleum (1·1 g) was evaluated by TLC on silica gel and found to contain in addition to *XXIII* and *XXIV* another component having the R_F between those of *XXIII* and *XXIV*. The mixture was dissolved in 6 ml boiling benzene and the solution allowed to crystallize at room temperature for 5 h. Filtration gave then further 0·30 g thioxanthone, m.p. 214—215°C. The filtrate was evaporated to a volume of 3 ml and allowed to crystallize for 48 h; 0·20 g, m.p. 175—179°C. This product is considered to be 9,9'-dithioxanthyl ether (*XXV*) on the basis of the mass spectrum and the analysis; it contains still some *XXIII* as an impurity. Mass spectrum, *m/e*: 410·0791 (M^+, corresponding to $C_{26}H_{18}OS_2$, calculated: 410·07918), 197 (thioxanthene radical), 212 (M^+ of thioxanthone as an impurity present). For $C_{26}H_{18}OS_2$ (410·4) calculated: 76·09% C, 4·42% H, 15·56% S; found: 76·12% C, 4·61% H, 15·84% S. The literature[10] reported first for the ether *XXV* a m.p. of 314—316°C; this was corrected, however, in a recent paper[11].

The authors are indebted to Dr J. Protiva, Charles University, Department of Organic Chemistry, Prague, and to Dr J. Schlanger (this Institute) for recording and interpretations of some of the mass spectra, to Mrs M. Hrubantová for technical assistance with the synthesis, and finally to Mrs J. Komancová, Mrs V. Šmídová, Mrs J. Kropáčová, Mr M. Čech and Mr K. Havel (department of ana-

lytical chemistry of this Institute) for carrying out the analyses. Our thanks are due to Dr H. Wolfram Fehlhaber, Spectroscopic Laboratory, Pharma-Synthese, Hoechst AG., Frankfurt/M. Germany, for his effort in helping us to elucidate the structure of our substance D by spectroscopic methods.

REFERENCES

1. Šindelář K., Protiva M.: Conf. Prague Section Czech. Chem. Soc., Zvíkovské Podhradí, November 1976; Abstracts of papers, p. 18.
2. Jílek J. O., Seidlová V., Svátek E., Protiva M.: Monatsh. Chem. *96*, 182 (1965).
3. Bickelhaupt F., Stach K., Thiel M.: Chem. Ber. *98*, 685 (1965).
4. Kraus M. in the book: *Preparativní reakce v organické chemii. IX. Isomerisace a degradace* (K. Kochloefl, M. Kraus, Eds), p. 115. Academia, Prague 1967.
5. Adams R., Reifschneider W., Nair M. D.: Croat. Chem. Acta *29*, 277 (1957).
6. Hanford W. E., Copenhaver J. W., Davis H. R. jr (M. W. Kellogg Co.): U.S. 2, 967. 887 (10. 01. 61); Chem Abstr. *55*, 12 337 (1961).
7. Šimůnek I., Kraus M.: This Journal *38*, 1786 (1973).
8. Jones R. G., Soper Q. F., Behrens O. K., Corse J. W.: J. Amer. Chem. Soc. *70*, 2843 (1948).
9. Campbell C. V. T., Dick A., Ferguson J., Loudon J. D.: J. Chem. Soc. *1941*, 747; Chem. Abstr. *36*, 1325 (1942).
10. Hilditch T. P., Smiles S.: J. Chem. Soc. *99*, 145 (1911).
11. Ivanov G. E., Izmailovskij V. A.: Zh. Org. Khim. *4*, 904 (1968); Chem. Abstr. *69*, 18 976 (1968).
12. Price C. C., Hori M., Parasaran T., Polk M.: J. Amer. Chem. Soc. *85*, 2278 (1963).
13. Ziegler J. H.: Ber. Deut. Chem. Ges. *23*, 2469 (1890).
14. Graebe C., Schulthess O.: Justus Liebigs Ann. Chem. *263*, 1 (1891); Ber. Deut. Chem.Ges. *24*, R 390 (1891).

Translated by the author (M. P.).