the one having m. p. 199–230°, the other m. p. 299–300° (3,6-dichlorofluorenone). There was no residue from these sublimates. This experiment indicates that while the rearrangement occurred at 125° it was not complete in forty minutes. As before the product of 3,6-dichlorofluorenone gave an oxime identical with authentic 3,6-dichlorofluorenone oxime.

1,6-Dichloro-4-aminofluorenone (X) and its Deamination.—Both the preparation and deamination of this amine have been described previously[1] (p. 4268) when the substance was derived from "Acid X." In this work the substance has been derived from 1,6-dichlorofluorenone-4-carboxylic acid which had been prepared from 5,5′-dichlorodiphenic acid.

The preparation of the amine was carried out by a modified method which gave much better results. Potassium hydroxide was used; the ratio of excess alkali to hypobromite was 3/1; the amide–hypobromite ratio was 1/1.2; the concentration of the hypobromite was about 0.0002 mole per cc. of solution; motor stirring was used. Recrystallization from benzene and ligroin gave the amine of m. p. 233–234°, dec. The deamination of this amine was carried out by the procedure previously described for the amine derived from "Acid X."

Summary

1. "Acid X," formed by the rearrangement of 1,6-dichlorofluorenone-5-carboxylic acid in sulfuric acid, is identical with 1,6-dichlorofluorenone-4-carboxylic acid formed when 5,5′-dichlorodiphenic acid is heated with sulfuric acid.

2. The temperatures at which the two isomeric dichlorofluorenone carboxylic acids (formed from 3,3′-dichlorodiphenic acid) are stable have been examined.

3. Phosphoric acid has been found to condense both the 3,3′- and the 5,5′-dichlorodiphenic acids but not to effect the *rearrangement* by which "Acid X" is produced.

4. Certain anomalous observations in the determination of the neutralization equivalent of "Acid X" appear to have been due to formation of solvates with the recrystallizing solvents.

5. "Acid X" has been decarboxylated directly by heating in sulfuric acid to give 3,6-dichlorofluorenone.

6. 1,6-Dichlorofluorenone and 1,8-dichlorofluorenone rearrange in hot concentrated sulfuric acid to give 3,6-dichlorofluorenone.

7. The condensations of other substituted diphenic acids and the rearrangements of the fluorenones and fluorenone carboxylic acids derived from them are being examined.

CAMBRIDGE, MASS. RECEIVED APRIL 10, 1936

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Properties of Unsaturated Sulfur Compounds. III. Alpha Beta Unsaturated Ketosulfones

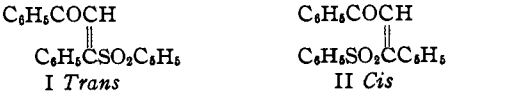
BY E. P. KOHLER AND R. G. LARSEN

In continuation of our investigation of unsaturated ketosulfones[1] we have prepared a representative in which one of the unsaturated carbon atoms holds both a phenyl and a phenylsulfonyl group, the relation between the present and the former sulfones being shown by the formulas

$C_6H_5COCH{=}C(C_6H_5)SO_2C_6H_5$ $C_6H_5COCH{=}CHSO_2C_6H_5$

The preparation of this substance enabled us to compare a number of similarly constituted compounds with respect to their stereoisomerism, the facility with which they enter into addition reactions and the mode of addition of unsymmetrical addenda.

The new ketosulfone, like the one described in the earlier paper, occurs in two forms of which one is yellow and the other colorless. From the analogy with the most closely related compounds of which the configuration is known—dibenzoyl ethylene and phenyl-β-benzoylpropionic ester—one would expect the polar groups to be in the *trans* position in the more stable yellow form. We therefore represent this form with I and designate it the *trans* compound.



I *Trans* II *Cis*

The relative melting points and solubilities of the two forms are the reverse of those of the unphenylated ketosulfones but the relative stabilities remain the same; a trace of base immediately produces a yellow color in solutions of the *cis* compound and in a short time converts it completely into the *trans* isomer. Owing to the reversal of the solubilities the effect of exposing concentrated solutions of the unphenylated and phenyl-

(1) Kohler and Larsen, THIS JOURNAL, **57**, 1448 (1935).

ated compounds to sunlight is quite different; in the case of the former the *trans* compound is converted practically completely into the *cis* while in the case of the latter both forms are converted into an equilibrium mixture containing but little of the *cis* compound.

Nearly all methods of preparation yield only the *trans* compound but when benzene sulfinic acid is added to benzoyl phenylacetylene the *cis* compound is formed exclusively. The two stereoisomers add other substances with practically the same ease. Both are easily oxidized and reduced and both also add halogen acids rapidly. As this easy addition of halogen acids was rather surprising it was important to establish the mode of addition with certainty. To this end we prepared one of the possible hydrogen bromide addition products by a method which was certain to give a compound of known structure, namely, by the addition of benzene sulfinic acid to α-bromo benzalacetophenone. The two diastereomeric bromo compounds obtained by this reaction were quite different in chemical and physical properties from the product obtained by adding hydrogen bromide to the unsaturated ketosulfone. The relations are shown by the following equations

$$C_6H_5COCH{=}C(C_6H_5)SO_2C_6H_5 + HBr \longrightarrow C_6H_5COCH_2CBr(C_6H_5)SO_2C_6H_5 \quad III$$

$$C_6H_5COCBr{=}CHC_6H_5 + C_6H_5SO_2H \longrightarrow C_6H_5COCHBrCH(C_6H_5)SO_2C_6H_5$$

These results show that the additional phenyl group has but little effect on the ease and none at all on the mode of addition of hydrogen compounds. In contrast it greatly affects both the facility and mode of addition of Grignard reagents. As a consequence of the accumulation of groups in the β position the primary reaction between the phenylated ketosulfone and phenylmagnesium bromide is addition to carbonyl. By operating with excess of reagent and at a higher temperature it is possible to add a second molecule of the reagent but the mode of addition is the reverse of that which occurs with the unphenylated ketosulfone. The two compounds which can be obtained in this manner are represented by the formulas

$$(C_6H_5)_2C(OH)C{=}(C_6H_5)SO_2C_6H_5 \quad IV$$

$$(C_6H_5)_2C(OH)CH(C_6H_5)CHSO_2C_6H_5 \quad V$$

The first of these substances is of special interest in connection with the peculiar behavior of the corresponding unphenylated compound $(C_6H_5)_2C(OH)CH{=}CHSO_2C_6H_5$.[2] The phenylated compound does not exhibit these peculiarities. All samples melt at the same temperature and decompose at the same rate regardless of origin and subsequent treatment. The substance not only does not itself undergo the allylic rearrangement but there also is no indication of rearrangement in metathetical reactions involving the hydroxyl group as, for example, when it is converted into its ethers, esters or chloride.

$$(C_6H_5)_2C(OCH_3)CH{=}C(C_6H_5)SO_2C_6H_5 \quad VI$$

$$(C_6H_5)_2C(OCOCH_3)CH{=}C(C_6H_5)SO_2C_6H_5 \quad VII$$

$$(C_6H_5)_2CClCH{=}C(C_6H_5)SO_2C_6H_5 \quad VIII$$

The structure of the products IV, VI and VII was established conclusively. Thus the carbinol IV on catalytic hydrogenation gives the same

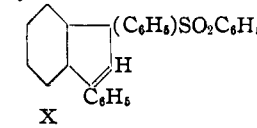
$$(C_6H_5)_2C(OH)CH{=}C(C_6H_5)SO_2C_6H_5 \quad (IV) \qquad C_6H_5COCH_2CH(C_6H_5)SO_2C_6H_5 \quad (A)$$

$$\longrightarrow (C_6H_5)_2C(OH)CH_2CH(C_6H_5)SO_2C_6H_5 \quad IX$$

saturated compound that is formed when the ketosulfone is first reduced and then treated with phenylmagnesium bromide.

The methyl ether VI can be oxidized to the corresponding ether of benzilic acid and the acetate VII reverts to the carbinol when it is hydrolyzed by weak acids—a process which is not accompanied by rearrangement. The structure of the chloro compound VIII was not established with the same certainty but its properties and its relations to other members of the series are in accord with the formula. Above its melting point it loses hydrogen chloride rapidly and passes into an indene derivative—presumably by way of an intermediate allene.

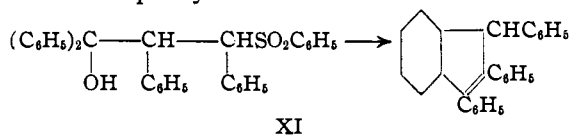
$$(C_6H_5)_2CClCH{=}C(C_6H_5)SO_2C_6H_5 \longrightarrow$$



X

(2) In the earlier paper it was assumed that this compound spontaneously undergoes an allylic rearrangement into an isomer which decomposes at a lower temperature. As a result of a physical investigation of the two products—which is described in the following paper by H. E. Bent and his collaborators—this interpretation is no longer tenable.

While the mode of addition of the first molecule of the Grignard reagent is evidently due to the properties of the conjugated system C=C—C=O, that of the second depends on the character of the system C=C—SO_2. The structure of the di-addition product was established by converting it into a known triphenylindene



XI

The foregoing account shows that the introduction of a phenyl group in the β position of an α,β unsaturated ketosulfone does not greatly affect its chemical properties. Except in the case of Grignard reagents the mode of addition is dependent on the character of the conjugated system C=C—C=O and the properties of the addition products express the tendency to revert to this system.

Experimental

The unsaturated ketosulfone was made from benzalacetophenone in a series of steps which can be represented as follows

$$C_6H_5COCH{=}CHC_6H_5 \longrightarrow C_6H_5COCH_2CH(C_6H_5)SO_2C_6H_5 \longrightarrow$$
A
$$C_6H_5COCHBrCH(C_6H_5)SO_2C_6H_5 \longrightarrow$$
B
$$C_6H_5COCH{=}C(C_6H_5)SO_2C_6H_5$$
I

The saturated ketosulfone (A) had been made previously by Posner[3] by adding thiophenol to benzalacetophenone and oxidizing the addition product to the sulfone but we found it simpler as well as more economical to form the sulfone in a single step by adding benzene sulfinic acid. The structure of the bromo compound (B) was established definitely by a synthesis which gives a compound of known structure, namely

$$C_6H_5COCBr{=}CHC_6H_5 + HSO_2C_6H_5 \longrightarrow C_6H_5COCHBr{-}CH(C_6H_5)SO_2C_6H_5$$

α-Phenyl-β-benzoyl Ethyl Phenyl Sulfone (A).—Equimolar quantities of ketone and pure sulfinic acid were brought together in concentrated alcoholic solution. The mixture evolved heat and soon solidified. One recrystallization from alcohol gave a product which melted at 159°. The yield was 93%.

α-Phenyl-β-bromo-β-benzoyl Ethyl Phenyl Sulfone (B).—The bromination of the ketosulfone in chloroform presented no difficulty; once the reaction was started it proceeded smoothly at the ordinary temperature until one mole of bromine had disappeared. The crystalline product that remained after removing the chloroform was subjected to fractional crystallization from methyl alcohol, and was thus eventually separated into two diastereomeric bromo compounds. The principal product, obtained in a yield of 90%, crystallized in coarse needles and melted at 189°. The second product, the yield of which was less than 3%, crystallized in very fine needles and melted at 209°.

Anal. Calcd. for $C_{21}H_{17}O_3BrS$: C, 58.8; H, 3.9. Found: (189°) C, 58.5; H, 4.0. (209°) C, 58.9; H, 4.2.

For the purpose of establishing the structure of these compounds concentrated solutions of equimolar quantities of α-bromo benzalacetophenone and benzene sulfinic acid in ethyl alcohol were kept at the ordinary temperature. In the course of several days the bromo compound melting at 209° crystallized from the solution.

α-Phenyl-β-benzoyl Vinyl Phenyl Sulfone I.—Both of the β-bromo derivatives of the saturated sulfone lose hydrogen bromide slowly when boiled with excess of potassium acetate in methyl alcohol or in acetic acid. In methyl alcohol the reaction with the compound melting at 189° was complete after the solution had been boiled for eighteen hours while that of the higher melting bromo compound required three days. In both cases the product was the yellow *trans* compound. It separated in yellow prisms which after recrystallization from methyl alcohol melted at 151°. The yield was 72%.

Anal. Calcd. for $C_{21}H_{16}O_3S$: C, 72.4; H, 4.6. Found: C, 72.0; H, 4.7.

The Cis Unsaturated Sulfone II.—To a solution of 2.75 g. of benzoyl phenyl acetylene in hot methyl alcohol was added 2.6 g. of benzene sulfinic acid. The mixture was boiled for a short time, then set aside. It yielded 2.8 g. of a colorless product a part of which crystallized from the solution while the remainder was obtained on evaporation. The *cis* compound crystallizes from methyl alcohol in colorless prisms and it melts at 132°.

Anal. Calcd. for $C_{21}H_{16}O_3S$: C, 72.4; H, 4.6. Found: C, 72.0; H, 4.7.

Attempts to ozonize the unsaturated sulfones were unsuccessful. Both forms reduce permanganate in acetone rapidly, being oxidized to two molecules of benzoic acid and one of benzene sulfonic acid. Both forms can also be reduced catalytically and with zinc and acid. Catalytic reduction is extremely slow and incomplete, doubtless because there is some elimination of benzene sulfinic acid which poisons the catalyst. Zinc and acetic acid, however, rapidly reduce the unsaturated sulfones to the same saturated compound.

Interconversion of the Two Isomers by Light.—A solution of 6 g. of the *trans* compound, and a little iodine, in chloroform was exposed to sunlight for three days in a quartz apparatus. At the end of the first day one-third of the solution was evaporated to dryness. The residue, separated by extraction and crystallization from methyl alcohol, was found to contain 0.2 g. of the *cis* compound—indicating about 10% conversion. A similar procedure at the end of the second and third days, gave in each case nearly 0.3 g. of the *cis* compound. In the reverse operation, carried out in the same way but starting with one gram of the *cis* form, the residue after exposure for three days contained 0.85 g. of *trans* and 0.13 g. of *cis*.

Isomerization with Chemicals.—A small drop of sodium methylate was added to a warm solution of 0.5 g. of the

(3) Posner, *Ber.*, **35**, 810 (1902).

cis compound. The mixture was left to itself for ten hours, then evaporated in a current of air. It left 0.48 g. of *trans* compound and a trace of oil. A similar solution when treated with a little methyl alcoholic solution of hydrogen chloride turned yellow and deposited some *trans* compound but most of the acid was removed by addition.

Addition of Hydrogen Bromide: α-Bromo-α-phenyl-β-benzoyl Ethyl Phenyl Sulfone, III.—A solution of the *trans* sulfone in glacial acetic acid was saturated with hydrogen bromide and left in an ice-box for thirty-six hours. As nothing separated from the solution it was diluted with ether, and freed from acid by washing with water and dilute bicarbonate. The dried ethereal solution, on concentration, deposited the bromide in large needles which, after recrystallization from methyl alcohol, melted with decomposition at 124°.

Anal. Calcd. for $C_{21}H_{17}O_3BrS$: C, 58.8; H, 3.9. Found: C, 59.0; H, 4.0.

The bromo compound is much less stable than the isomeric β-bromo derivative. At the melting point it rapidly loses hydrogen bromide and reverts to the *trans* unsaturated sulfone and when its alcoholic solutions are boiled they gradually turn yellow in color and become acidic.

The corresponding chloro compound—prepared in the same way—is more stable. It crystallizes in colorless needles and melts at 175°.

Anal. Calcd. for $C_{21}H_{17}O_3ClS$: C, 65.5; H, 4.4; Cl, 9.2. Found: C, 65.6; H, 4.6; Cl, 9.1.

Addition of Phenylmagnesium Bromide: the Mono-addition Product.—To an ethereal solution which contained four times the calculated quantity of reagent and which was cooled in ice, was added 7 g. of finely powdered yellow sulfone. The mixture was stirred vigorously for several hours, then decomposed with iced ammonium chloride solution. The product crystallized with two molecules of methyl alcohol in large colorless prisms melting at about 107°. Heated to 100° under diminished pressure, the crystals lost methyl alcohol and passed into a powder melting at 133°.

Anal. Calcd. for $C_{27}H_{22}O_3S \cdot 2CH_3OH$: C, 71.0; H, 6.1. Found: (Prisms) C, 71.2; H, 6.1. Calcd. for $C_{27}H_{22}O_3S$: C, 76.2; H, 5.4. Found: (Powder) C, 76.0; H, 5.1.

Reduction: α-Phenyl-γ-hydroxy-γ,γ-diphenyl Propyl Phenyl Sulfone, IX.—Catalytic hydrogenation with platinum oxide was almost impossible because of the rapidity with which the catalyst was poisoned. With palladium on calcium carbonate, however, the hydrogenation was accomplished without much difficulty, the sparingly soluble product separating from the ethyl acetate used as solvent as fast as it was formed. It crystallized in thin needles melting at 223°. The same compound was obtained, in a yield of 75%, when phenylmagnesium bromide was added to the saturated ketosulfone.

Anal. Calcd. for $C_{27}H_{24}O_3S$: C, 75.7; H, 5.6. Found: C, 75.5; H, 5.6.

The Methyl Ether, VI.—A drop of acetyl chloride was added to a solution of the unsaturated carbinol in boiling methyl alcohol and the solution was then allowed to evaporate in a current of air. It deposited the ether in hexagonal tables melting at 130°.

Anal. Calcd. for $C_{28}H_{24}O_3S$: C, 76.4; H, 5.5. Found: C, 76.6; H, 5.6.

Oxidation.—A dilute solution of the ether in acetone was acidified with a little acetic acid, then treated with the calculated quantity of permanganate in acetone and set aside until completely decolorized. Among the neutral products isolated by the usual manipulations was a substance which crystallized in needles melting at 100° and which was identified as the methyl ether of benzilic acid by comparison with a sample prepared directly from benzilic acid. The yield was 30%.

The Acetate, VII.—A solution of the mono-addition product in acetic anhydride was boiled for four hours, then cooled and poured into water. From the resulting suspension ether extracted a solid which recrystallized from absolute methyl alcohol in needles melting at 168°.

Anal. Calcd. for $C_{29}H_{24}O_4S$: C, 73.7; H, 5.3. Found: C, 73.7; H, 5.4.

The acetate was not affected by boiling water but when it was hydrolyzed with methyl alcoholic potassium hydroxide it reverted to the carbinol and when it was boiled with methyl alcohol that contained a trace of acetic acid it was slowly converted into the methyl ether.

α-Phenyl-γ-chloro-γ,γ-diphenyl Propyl Phenyl Sulfone, VIII.—Dry hydrogen chloride was passed through a solution of the carbinol in benzene until the turbidity, caused by the separation of water, was removed. The solution was then allowed to evaporate spontaneously and the residual green oil was diluted with dry ether. It deposited the chloride in long colorless needles which after recrystallization from dry ether melted with decomposition at about 142°. The yield was quantitative.

Anal. Calcd. for $C_{27}H_{21}OSCl$: C, 72.9; H, 4.8. Found: C, 72.4; H, 5.0.

The chloro compound is stable in the air. When it is boiled with methyl alcohol or with methyl alcoholic potassium acetate it is converted into the ether. Potassium acetate in glacial acetic acid converts it into the acetate.

1,3-Diphenyl-3-phenylsulfonyl Indene, X.—The chloro compound which has just been described loses hydrogen chloride rapidly at the melting point. The residue is an amber colored liquid that is readily soluble in ether. The ethereal solution gradually deposits colorless needles melting at 171°.

Anal. Calcd. for $C_{27}H_{20}O_2S$: C, 79.4; H, 4.9. Found: C, 79.2; H, 5.1.

In proof that the product is an indene derivative 1 g. was oxidized with 1.5 g. of sodium dichromate in glacial acetic acid. The product, isolated in the usual manner, was ortho dibenzoyl benzene—identified by comparison with an authentic sample. The yield was 70%.

α,β,γ,γ-Tetraphenyl-γ-hydroxy Propyl Phenyl Sulfone, V.—To an ethereal solution of phenylmagnesium bromide prepared from 2.25 g. of magnesium was added 10 g. of finely powdered unsaturated ketosulfone. The mixture was boiled for two hours, then cooled and decomposed with iced acid. A part of the product was deposited during the acidification, the remainder being isolated by the usual manipulations of the solution. Three substances were obtained in this manner, namely: the mono-addition product (57%), a di-addition product melting at 178°

(15%), and a stereoisomeric di-addition product melting at 223° (12%). In a similar experiment in which the reacting mixture was boiled for six hours the yields were 22% of mono-addition product, 26% of product melting at 178° and 32% of product melting at 196°. Both of the di-addition products are sparingly soluble in common organic solvents. The lower melting—which is the less soluble—crystallizes from acetone in small prisms and the higher melting crystallizes in six-sided tables containing acetone of crystallization.

Anal. Calcd. for $C_{38}H_{28}O_3S$: C, 78.6; H, 5.6. Found: C, 78.6; H, 6.0. Calcd. for $C_{33}H_{28}O_3S \cdot C_3H_6O$: C, 77.1; H, 6.0; C_3H_6O, 10.3. Found: C, 77.1; H, 5.7; C_3H_6O, 10.1.

The structure of the di-addition products was established by converting them into triphenyl indene. To this end a solution of each in glacial acetic acid containing a small quantity of sulfuric acid was heated on a steam-bath for half an hour, then diluted first with methyl alcohol and finally with water. In each case the product was identified by comparison with a sample on hand.

Summary

The paper contains a comparison of $C_6H_5COCH=C(C_6H_5)SO_2C_6H_5$ and $C_6H_5COCH=CHSO_2C_6H_5$ with respect to their stereoisomerism, the facility with which they enter into addition reactions, the mode of addition of hydrogen compounds and the mode of addition of Grignard reagents.

CAMBRIDGE, MASS. RECEIVED JUNE 3, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Physical Investigation of β-Hydroxy-β,β-diphenylvinyl Phenyl Sulfone

BY H. E. BENT, E. S. LARSEN AND H. BERMAN

In a recent paper Kohler and Larsen[1] described two compounds which "are interesting by reason of the very remarkable ease with which they undergo the allylic rearrangement.... Most solutions, on chilling, deposit a mixture of both isomers but by slow crystallization from properly selected solvents it is possible to secure both isomers in a pure condition—the tertiary alcohol VIII from benzene and the secondary alcohol X from methyl or ethyl alcohol." The tertiary alcohol, β-hydroxy-β,β-diphenylvinyl phenyl sulfone, has the structure $(C_6H_5)_2C(OH)-CH=CHSO_2C_6H_5$ and the secondary alcohol, α-hydroxy-β,β-diphenylpropenyl phenyl sulfone, X, has the structure $(C_6H_5)_2C=CH-CH(OH)SO_2C_6H_5$. The melting point of the tertiary alcohol is given as 193° and of the secondary alcohol as 164°. Both compounds crystallize readily but differ greatly in appearance. This apparent reversal of the direction of transformation by different solvents at the same temperature is, however, thermodynamically impossible, and we have therefore reëxamined more carefully the physical properties of these two substances.

Crystallographic measurements were made as follows:

(1) Kohler and R. G. Larsen, THIS JOURNAL, 57, 1448 (1935).

OPTICAL CRYSTALLOGRAPHY

	Cpd. VIII	Cpd. X
α	1.608	1.607
β	1.656	1.657
γ	1.710	1.706
Opt. sign	(+) $2V$ med.	(+) $2V$ med.
Orientation	$Z = b$	$Z = b$
	$X\wedge C = 23°$	$X\wedge C = 23°$

CRYSTALLOGRAPHY

Measurements on X

Forms: (010)(100)(110)(011)(101) Monoclinic-holohedral

$a:b:c = 1.0597:1:0.3277$ $\beta = 99° 05'$

$p_0 = 0.30926$ $q_0 = 0.32362$ $e = 0.15784$

Form	Observed (averages) ϕ	Observed (averages) ρ	Calculated ϕ	Calculated ρ	Number of observations
(010)	0°	90° 00′	0°	90° 00′	4
(100)	90° 00′	90° 00′	90° 00′	90° 00′	1
(110)	43° 42′	90° 00′	43° 42′	90° 00′	12
(011)	26° 00′	20° 02′	26° 00′	20° 02′	6
(101)	90° 00′	25° 17′	90° 00′	25° 19′	1
Ranges: for (110)			43° 32′ to 43° 55′		
(011)			25° 40′ to 26° 41′		19° 47′ to 20° 10′

Measurements on a single crystal of VIII

Form	ϕ	ρ
(010)	0°	90° 00′
(110)	39° 49′	90° 00′
(011)	25° 51′	20° 09′

Crystals X are much superior in quality and the angles of these are to be relied upon for a good axial ratio for the substance. Crystals VIII were difficult to measure since they were of the order of 0.1 mm. in maximum size. Several crystals