thirty minutes longer at $-10°$ and then poured onto 150 g. of ice. The excess acid was carefully neutralized with 40% sodium hydroxide and the mixture extracted with ether. The extract was immediately treated with 20 ml. of pyridine and allowed to stand for twelve hours in the refrigerator. Removal of the solvent and acidification of the residue with an excess of ice cold 10% hydrochloric acid gave the crude ester, which after crystallization from methanol, weighed 5 g. and melted at 42°.

Anal. Calcd. for $C_8H_9O_5N$: C, 48.24: H, 4.52. Found: C, 48.15: H, 4.71.

The ester was hydrolyzed by refluxing for two hours with a solution of 10 g. of sulfuric acid and 25 ml. of water. The acid melted at 194° after crystallization from water.

Anal. Calcd. for $C_6H_5O_5N$: C, 42.10: H, 2.92. Found: C, 41.93: H, 3.08.

This acid may also be obtained by direct nitration of 3-methyl-4-furoic acid. Twelve and one-half grams of the acid was added portionwise at $-15°$ to a stirred nitrating mixture prepared from 36.6 g. of nitric acid (sp. gr. 1.51) and 78 ml. of acetic anhydride. The mixture was stirred for one hour longer at $-10°$, poured onto 500 g. of ice and extracted with ether. The solvent was evaporated and the crude product crystallized from water to give 4.2 g. of the acid melting at 193°.

2-Nitro-3-methylfuran-4,5-dicarboxylic Acid.—Five grams of dimethyl 3-methylfuran-4,5-dicarboxylate was added in small portions with stirring at $-10°$ to a nitrating mixture composed of 7.9 g. of nitric acid (sp. gr. 1.51) and 12 ml. of acetic anhydride. Stirring was continued for one hour at $-10°$, followed by dilution with ice, extraction and treatment with pyridine as previously described. The crude nitro ester was hydrolyzed by refluxing for seven hours with a solution of 10 g. of sulfuric acid and 25 ml. of water. After treatment with decolorizing charcoal the hot filtrate was chilled to give the crude acid. Crystallization from benzene yielded 1.5 g. of the acid melting at 218°.

Anal. Calcd. for $C_7H_5O_7N$: C, 38.88: H, 2.31: neut. equiv., 108. Found: C, 38.78: H, 2.81: neut. equiv., 107.3.

Decarboxylation of 2-Nitro-3-methylfuran-4,5-dicarboxylic Acid.—One-tenth gram of the dicarboxylic acid contained in a long, narrow test-tube was heated in a metal-bath at 225°. Carbon dioxide was evolved, and a white crystalline solid condensed on the upper walls of the

tube. This material melted at 194° and showed no depression in melting point when mixed with samples of 2-nitro-3-methyl-4-furoic acid previously described.

Dimethyl 2-Nitrofuran-4,5-dicarboxylate.—A solution of 6.2 g. (0.033 mole) of dimethyl furan-2,3-dicarboxylate[4] in 9 ml. of acetic anhydride was added dropwise at $-10°$ to a stirred nitrating mixture prepared from 10.3 g. (0.16 mole) of nitric acid (sp. gr. 1.51) and 15.6 ml. of acetic anhydride. The mixture was stirred for an additional hour at $-10°$, poured onto ice, neutralized with caustic solution, extracted with ether and the extract treated with 20 ml. of pyridine. After twelve hours of storage in the refrigerator the solvent was removed and the residue suspended in an excess of ice-cold 10% hydrochloric acid. The crude product thus obtained was crystallized from methanol to give 5.1 g. of the nitro ester melting at 97°.

Anal. Calcd. for $C_8H_7O_7N$: C, 41.92: H, 3.05. Found: C, 42.15: H, 3.79.

Decarboxylation of 2-Nitrofuran-4,5-dicarboxylic Acid.—Four grams of the above ester was hydrolyzed by refluxing for four hours with a solution of 12 g. of sulfuric acid and 24 ml. of water. The chilled hydrolysate was washed once with chloroform to remove any unchanged ester and then extracted thoroughly with ether. Evaporation of the solvent yielded the crude 2-nitrofuran-4,5-dicarboxylic acid, which after crystallization from a mixture of ether and benzene melted at about 225° with gas evolution.

This material contained in a long, narrow test-tube was heated in a metal-bath at 235°. Carbon dioxide was evolved and a white crystalline solid deposited on the upper part of the tube. Resublimation followed by crystallization from water afforded an acid melting at 137°, which was identical with that obtained by the direct nitration of 3-furoic acid.[2]

Summary

Bromination of 3-methyl-4-furoic acid, mercuration of the methyl ester, and nitration of the ethyl ester result in substitution in the 2-position. The structure of 2-nitro-4-furoic acid has been established.

(4) Asahina, *et al.*, *Acta Phytochim.*, **2**, 1 (1924).

The Ultraviolet Absorption Spectra of Aliphatic Sulfides and Polysulfides[1]

By John E. Baer[2] and Marvin Carmack

Various organic polysulfides, RS_xR', have been prepared in which R and R' are simple alkyl groups.[3] Recently interest has been aroused in the 2-chloroethyl polysulfides in connection with the characterization of the by-products of the manufacture of mustard gas by the Levinstein

process.[4,5] Other aliphatic polysulfides of particular interest are the Thiokol types of elastomers and possible intermediates in the vulcanization of rubber.

In view of the differing opinions regarding the manner of attachment of the sulfur atoms in the organic polysulfides, new methods for the recognition of different types of linkages are of interest, particularly methods which do not alter the polysulfide groups chemically.

We have found that aliphatic polysulfides have intense and characteristic ultraviolet absorption

(1) The essential material of this paper was presented before the Organic Division of the American Chemical Society at the National Meeting in Chicago, Illinois, April 22, 1948. It is from the Ph.D. dissertation of John E. Baer, accepted by the Faculty of the Graduate School of Arts and Sciences of the University of Pennsylvania, June, 1948.

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(3) R. Connor, "Organic Chemistry," (ed. H. Gilman), John Wiley and Sons, New York, N. Y., ed. 2, 1943, Vol. I, p. 864.

(4) Fuson, Price, Burness, Foster, Hatchard and Lipscomb, *J. Org. Chem.*, **11**, 487 (1946).

(5) Macy, Jarman, Morrison and Reid, *Science*, **106**, 355 (1947).

spectra. The locations of the peaks and the intensities differ widely depending upon the number of sulfur atoms in the polysulfide function. Consequently, the preliminary results suggest that spectrometric measurements may afford a convenient method for the qualitative identification of different types of polysulfides. In some cases, also, absorption spectrometry may be applied to the analysis of mixtures.

We were led to investigate the absorption spectra of polysulfides by the following considerations. (1) Simple mercaptans and alkyl sulfides, unlike most organic compounds containing no multiple linkages, show a characteristic sharp absorption band in the far ultraviolet region (near 200 mμ).[6] Appearance of such a peak indicates that the unshared electrons of the sulfur atom can be excited by frequencies of light possessing about the same energy as those which excite the carbon-carbon double bond. (2) Many chemical analogies between the —S̈— and the —C̈=C̈— groups have been observed and classified under the general term, isosterism, based upon similarities in the electronic systems. (3) Resonance forms of com-

pounds containing the —S̈— function have been postulated[7] in which the sulfur atom expands its valence shell to ten or more electrons: such assumptions are considered necessary to account for dipole moments and other physical and chemical properties of certain sulfur-containing compounds.

The facts cited above lead one to expect that, in the disulfides and polysulfides, the groupings of linked sulfur atoms will behave optically somewhat like conjugated systems of carbon–carbon double bonds, as, for example, in the conjugated polyene hydrocarbons. That is, the peak of light absorption will increase in intensity and shift toward longer wave lengths as the number of conjugated sulfur atoms in the functional group increases. Some evidence of conjugation between sulfide groups and other functional groups containing double bonds has been noted in other connections in This Laboratory.[8]

Crystalline n-hexadecyl trisulfide and n-hexadecyl tetrasulfide[9] were chosen as particularly suitable reference compounds. Since these two compounds can be readily synthesized in good yields by straightforward methods and give the ordinary indications of homogeneity (sharpness and reproducibility of melting points and constancy of composition), there is little reason to doubt their true polysulfide nature and freedom from contamination with elementary sulfur. Furthermore, n-hexadecyl disulfide, n-hexadecyl sulfide, and n-hexadecyl mercaptan are all available and are well-defined, low-melting crystalline solids,[10] readily soluble in paraffinic solvents in which ultraviolet absorption spectra are relatively little complicated by solvent effects.

Figure 1 shows the absorption spectra of RSH (I) (R = n-C$_{16}$H$_{33}$), R$_2$S (II), R$_2$S$_2$ (III), R$_2$S$_3$ (IV), R$_2$S$_4$ (V), and S$_8$ (VI) in hexane. The mercaptan and sulfide have spectra very similar to other simple alkyl compounds with these functional groups.[6,8] The mercaptan spectrum shows the typical shoulder at 225 mμ which has been noted with other mercaptans.[1] The absorption maxima for I and II lie just beyond the limits accessible to measurement with the instrument and solvent used. The disulfide (III) exhibits a fairly intense new peak at 252 mμ (log ϵ 2.63), an indication of conjugation between the unshared electrons on the two sulfur atoms.[11]

The trisulfide (IV) has two maxima: 251 mμ (log ϵ 3.22) and 213 mμ (log ϵ 3.87). The absorp-
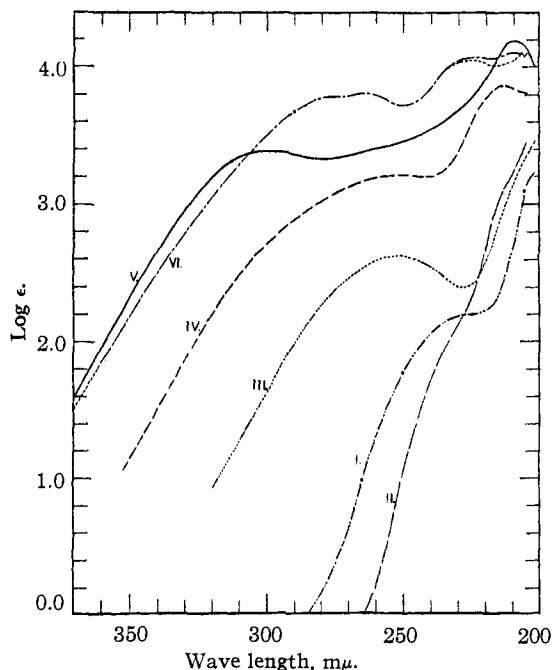

Fig. 1.—Curve I, n-hexadecyl mercaptan; II, n-hexadecyl sulfide; III, n-hexadecyl disulfide; IV, n-hexadecyl trisulfide; V, n-hexadecyl tetrasulfide; VI, sulfur (S$_8$) in hexane and alcohol (except dotted portion below 230 mμ showing deviation in alcohol).

(6) (a) Purvis, Jones and Tasker, *J. Chem. Soc.*, **97**, 2287 (1910); (b) Hantzsch, *Ber.*, **52**, 1544 (1919); **58**, 612 (1925); (c) Gibson, Graham and Reid, *J. Chem. Soc.*, **123**, 874 (1923); (d) Houston, Canning and Graham, *ibid.*, 965 (1935); (e) Ley and Arends, *Z. physik. Chem.*, **B15**, 311 (1932); (f) Price, *J. Chem. Phys.*, **3**, 256 (1935); (g) Mohler and Sorge, *Helv. Chim. Acta*, **23**, 1200 (1940); Mohler, *ibid.*, **20**, 287, 1188 (1937).

(7) Schomaker and Pauling, THIS JOURNAL, **61**, 1769 (1939).

(8) Fehnel and Carmack, *ibid.*, **71**, 84, 231 (1949).

(9) Clayton and Etzler, *ibid.*, **69**, 974 (1947).

(10) (a) Collin, Hilditch, Marsh and McLeod, *J. Soc. Chem. Ind.*, **52**, 272T (1933); (b) Flaschentröger and Wannschaff, *Ber.*, **67**, 1121 (1934).

(11) Ethyl disulfide has an absorption band with a maximum at 249 mμ (log ϵ 2.63) (ref. 6e). Cystine has also been reported to exhibit a similar peak. Anslow and Foster, *J. Biol. Chem.*, **97**, 37 (1932).

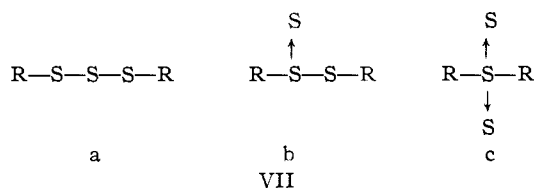tion is much more intense for the trisulfide than for the disulfide.[12]

The tetrasulfide (V) shows two maxima: 300 mμ (log ϵ 3.39) and 209 mμ (log ϵ 4.19). The whole absorption curve for the tetrasulfide is more intense than that of the trisulfide, and the first peak is shifted markedly toward the visible region compared with the trisulfide.

The absorption spectrum of solutions of molecular sulfur is of interest not only to permit an evaluation of its contribution to the absorption of mixtures in which it may be present, but also because the ordinary S_8 molecule provides a structural model in which the mode of attachment of multiple units of sulfur atoms has been established by independent methods[13] and in which even the geometric relationships are well defined. The structure is considered to be a puckered eight-membered ring, as represented by formula VI.

$$\begin{array}{c} \text{S---S} \\ \text{S} \qquad \text{S} \\ \text{S} \qquad \text{S} \\ \text{S---S} \end{array} \quad \text{(VI)}$$
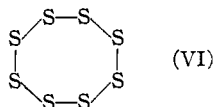
Curve VI of Fig. 1 shows the spectra of solutions of sulfur as determined in both hexane and ethyl alcohol. Curves in the two solvents are identical over a wide range, but differ slightly at short wave lengths. Several peaks and plateaus of high intensity are so broad and tend to merge to such an extent that the determination of the exact locations of the maxima is difficult. It may be noted that the absorption spectra of S_8 and of n-hexadecyl tetrasulfide have certain features in common: namely, both are nearly congruent from the visible region to approximately 320 mμ, and extinction values are of the same order of magnitude through the whole range investigated.

Several structures have been suggested for organic trisulfides (VIIabc)[3,4,5,14,15]; most authorities have favored the linear formulation (VIIa).[3,4]

$$\begin{array}{ccc}
& \text{S} & \text{S} \\
& \uparrow & \uparrow \\
\text{R---S---S---S---R} \quad & \text{R---S---S---R} \quad & \text{R---S---R} \\
& & \downarrow \\
& & \text{S} \\
a & b & c
\end{array}$$

VII

Recent studies of methyl trisulfide[15] by means of electron diffraction support the linear formulation.

A number of possible structures can be written for tetrasulfides, but the three formulas most seriously considered have been VIIIabc.

$$\begin{array}{ccc}
\text{S} & \text{S} \quad \text{S} \\
\uparrow & \uparrow \quad \uparrow \\
\text{R---S---S---S---S---R} \quad \text{R---S---S---S---R} \quad \text{R---S---S---R} \\
a \qquad\qquad b \qquad\qquad c
\end{array}$$

VIII

In the conjugated diphenylpolyene series, $C_6H_5(CH=CH)_nC_6H_5$, a relationship has been found between the value of n and λ^2 for the first absorption band.[16] It might be expected that chains of sulfur atoms connected linearly as in the series $R-(-S-)_nR$ would show a regular shift of absorption maxima with increasing values of n, and that attachment of sulfur atoms along the chain in a non-linear fashion (as in VIIbc and VIIIbc) would be revealed by irregularities which could be correlated with structure.[17]

The correlation of structure with spectra in the polysulfide series is obviously very complicated, and many more compounds will need to be prepared before the relationships can be fully interpreted. It seems likely, for example, that steric relationships among the sulfur atoms of a polysulfide group may have an important influence upon the spectra. Zechmeister, LeRosen, Schroeder, Polgar and Pauling[18] have shown that in the carotenoid polyenes the stereochemical configurations have important, and predictable, influences upon the spectra. Similarly, in the polysulfides it may be expected that rigid polysulfide structures may have somewhat different spectra than acyclic polysulfides for which many stereochemical configurations are possible. The synthesis of other polysulfides, including the cyclic, is under investigation. Determinations of the spectra at lower temperatures may perhaps permit a sharper resolution of the absorption peaks.[19]

(12) That the trisulfide and disulfide should both have one peak at almost the same wave length (251–252 mμ) should probably not be considered particularly significant. The more intense peak of IV centering at 213 mμ has its foot superimposed upon the lower first absorption band, and this makes it difficult to estimate the location of the true center of the first absorption band. If merging of the broad bands did not occur to such an extent, it seems likely that the first band of the trisulfide would have a maximum somewhat nearer the visible region than the first band of the disulfide.
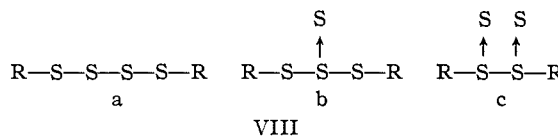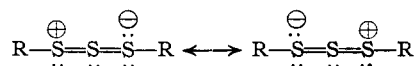
(13) Yost and Russell, "Systematic Inorganic Chemistry," Prentice–Hall, New York, N. Y., 1944, p. 277. Molecular extinction values were calculated on the basis of the molecular formula S_8 and it was assumed that the molecular state in solutions at room temperature is the same as in the crystalline state.

(14) Westlake, Mayberry, Whitlock, West and Haddad, THIS JOURNAL, 68, 748 (1946).

(15) Donohue and Schomaker, J. Chem. Phys., 16, 92 (1948).

(16) For an excellent recent discussion of this and other similar correlations of structure and spectra, cf., Maccoll, Quarterly Reviews of the Chemical Society (London), 1, No. 1, 16–58 (1947), especially p. 45.

(17) The assumption of an analogy between the optical behavior of polyene chains and linear polysulfide chains implies that polarization can occur by a transfer of charge along the chain of sulfur atoms. Polarization of the molecule can occur if one sulfur atom accepts an extra pair of electrons from its adjoining neighbor (thus expanding its valence shell to ten electrons). For example, in a linear trisulfide the polar forms could be written

$$\underset{\cdots \quad \cdots \quad \cdots}{\overset{\oplus \qquad \ominus}{\text{R---S}=\text{S}=\text{S}\text{---R}}} \longleftrightarrow \underset{\cdots \quad \cdots \quad \cdots}{\overset{\ominus \qquad \oplus}{\text{R---S}=\text{S}=\text{S}\text{---R}}}$$

The non-linear structures of polysulfides are generally written with semipolar bonds between the chain sulfur and the extra sulfur atoms, implying a permanent polarization of the molecule; however, if expansion of the sulfur valence shell is possible, then a large number of resonance forms can be written for the non-linear as well as for the linear structures.

(18) Zechmeister, LeRosen, Schroeder, Polgár and Pauling, THIS JOURNAL, 65, 1941 (1943).

(19) Scott, Sinsheimer and Loofbourow, Science, 107, 302 (1948).

Experimental

Preparation and Purification of Compounds.— *n*-Hexadecyl mercaptan purchased from the Connecticut Hard Rubber Company. m.p. 18°.[10b] was distilled at 0.6 mm., b.p. 135–140°. The middle cut was used for the spectrometric determination and for some of the other preparations described below. Analyses for carbon. hydrogen. and sulfur were satisfactory. *n*-**Hexadecyl sulfide** was prepared by the reaction of *n*-hexadecyl bromide[20] with sodium sulfide in alcohol: after recrystallization from 95% alcohol–hexane. colorless crystals. m.p. 58.2–58.5° (reported m.p. 57.5°[21]): analyses for carbon and hydrogen agreed with theory. *n*-**Hexadecyl disulfide** was prepared from *n*-hexadecyl mercaptan by oxidation with iodine in alcohol according to Collin *et al.*[10a]: recrystallization from acetone gave colorless needles. m.p. 55–55.5° (reported m.p. 54°[10a]). The sample for spectrometric analysis was recrystallized again from glacial acetic acid: analyses for carbon. hydrogen and sulfur agreed with the theoretical. *n*-**Hexadecyl trisulfide** was prepared from *n*-hexadecyl mercaptan and freshly redistilled sulfur dichloride according to the procedure of Clayton and Etzler[9]: recrystallization of the product from hexane–acetone gave colorless crystals. m.p. 42.0–42.6° (reported m.p. 41.2–41.9°[9]): analyses for carbon and hydrogen agreed with the theoretical. *n*-**Hexadecyl tetrasulfide** was prepared from *n*-hexadecyl mercaptan and sulfur monochloride according to the procedure of Clayton and Etzler[9]: recrystallization of the product three times from hexane–acetone gave a faintly yellow crystalline product. m.p. 36.8–37.2° (reported m.p. 35.9–36.5°[9]): analyses for carbon and hydrogen agreed with the theoretical. All preparations were repeated to verify the reproducibility of results. Sulfur (commercial, sublimed) was twice recrystallized from alcohol. m.p. 119° (capillary).

Determination of Ultraviolet Absorption Spectra.— The hexane used as a solvent in most of the determinations was purified by washing with 10% fuming sulfuric acid. followed by washing with aqueous sodium bicarbonate and water. then distillation through a Vigreux column. The

(20) Purchased from Halogen Chemicals. Inc.. Columbia. S. C.

(21) Fridau. *Ann.*, **83**, 16 (1852).

spectrum of sulfur was determined in Commercial Solvents Gold Shield Absolute Alcohol as well as in hexane. Differences in the spectra in the two solvents were only observed at wave lengths below 230 mμ. Measurements were made in the Beckman Model DU Quartz Spectrophotometer in 1-cm. quartz cells. Values of log ϵ in the range 1–2 were measured at 10^{-2} M concentration. log ϵ 2–3 at 10^{-3} M. log ϵ 3–4 at 10^{-4} M. etc. Wave bands did not exceed 2.3 mμ. Most curves were checked on two different preparations of the same compound.

Mixed Melting Point Determinations.—It was of interest to determine whether mixtures of the various polysulfides would show depressions of melting point. For each of the several pairs of compounds. four simultaneous capillary melting point observations were made: specimens of each pure compound. a 2:1 mixture. and a 1:2 mixture of the two. The mixture of 1 disulfide: 2 trisulfide showed a 1°-depression below the m.p. of the pure trisulfide. The mixtures of the disulfide and tetrasulfide melted over wide ranges between the limits for the pure compounds. Mixtures of the trisulfide and tetrasulfide melted over ranges at intermediate values.

Acknowledgment.—Analyses of all compounds were made by Mrs. Sarah Miles Woods.

Summary

The ultraviolet absorption spectra of *n*-hexadecyl mercaptan. *n*-hexadecyl sulfide. *n*-hexadecyl disulfide. *n*-hexadecyl trisulfide. and *n*-hexadecyl tetrasulfide were determined in hexane solution. The spectra of sulfur in hexane and in ethanol solutions were determined. The spectra of the polysulfides have been shown to vary markedly with the sulfur content of the functional group. Spectrometry may be useful in the qualitative identification and quantitative estimation of various organic polysulfides.

The Synthesis of tris-(Hydroxymethyl)-methylnitramine and Other Compounds Related to tris-(Hydroxymethyl)-aminomethane[1]

BY JAMES CASON[2] AND FRANKLIN S. PROUT[2a]

In connection with studies on nitramines carried out in this country and Canada it became desirable to study the absorption spectra of an aliphatic nitramine and the isomeric nitrosohydroxylamine. The present communication describes the synthesis of such an isomeric pair. The study of the absorption spectra is reported separately by other authors.[3]

Although there have been prepared. in the aromatic series. nitramines isomeric with known ni-

trosohydroxylamines[4] there appears to be no report of the preparation and isolation in a pure condition of such an isomeric pair in the aliphatic series. In fact. there have been reported only a limited number of aliphatic nitrosohydroxylamines which are sufficiently stable to permit isolation in a pure state. tris-(Hydroxymethyl)-methylnitrosohydroxylamine has been prepared by Piloty and Ruff.[5] starting with tris-(hydroxymethyl)-nitromethane, and this preparation has been repeated by us with some modifications.

The method first investigated for the preparation of the previously unknown tris-(hydroxy-

(1) This paper is based entirely on work done for the Office of Scientific Research and Development under Contract OEMsr-790 with Vanderbilt University.

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(3) Carmack and Leavitt. THIS JOURNAL. **71**. 1221 (1949).

(4) Hantzsch. *Ber.*, **31**. 177 (1898): **38**. 1000 (1905): Bamberger. *ibid.*, **27**. 363 (1894): **31**. 577 (1898): Bradfield and Orton. *J. Chem. Soc.*, 915 (1929): Marvel. "Org. Syn.." Coll. Vol. I. 177 (1941): Thiele. *Ann.*, **376**. 256 (1910): Neubauer. *ibid.*, **298**. 200 (1897).

(5) Piloty and Ruff. *Ber.*, **30**. 1656 (1897).