Anal. Calcd. for per cent nitrogen of the monomer ratio 3:7, 1.63%. Found: N, 1.11%.

Polymer 6 was a white powder; softened at 105°, had m.p. 120–125°, and a specific viscosity (1% in toluene) 0.45.

Anal. Calcd. for per cent nitrogen in the monomer ratio 6:4, 3.26%. Found: N, 1.56% (see Table VIII).

Acknowledgment. The authors gratefully acknowledge the able assistance with some of these preparations by Mr. D. H. Haigh and Mr. J. H. Penfold.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Orientation in the 10-Thiaxanthenone[1] Nucleus

HENRY GILMAN AND JUSTIN W. DIEHL

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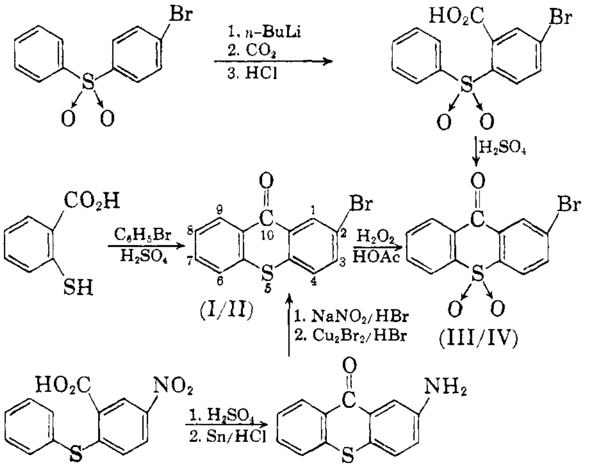
It has been found that cyclization by the procedure of Smiles of *o*-mercaptobenzoic acid with monosubstituted benzene derivatives in concentrated sulfuric acid leads to the formation of 10-thiaxanthenone compounds in which the substituent is in the 2-position. A mechanism incorporating a sulfenium ion accounts for these *o*-mercaptobenzoic acid cyclizations.

In the course of investigating the action of concentrated sulfuric acid on aromatic disulfides, Smiles[2,3] synthesized several substituted 10-thiaxanthenone derivatives. The position of the substituent has now been determined for some of these compounds.

Reaction of either 2,2′-dithiodibenzoic acid or *o*-mercaptobenzoic acid with bromobenzene in concentrated sulfuric acid gave a compound (I) with a melting point, 166–167°, which does not agree with that, 141°, reported for *x*-bromo-10-thiaxanthenone prepared initially by Smiles in an analogous manner.[3] The bromine atom was shown to be in the 2-position by the following sequence of reactions. A Sandmeyer reaction on 2-amino-10-thiaxanthenone[4] gave 2-bromo-10-thiaxanthenone (II) which showed no depression in melting point when admixed with the above *x*-bromo-10-thiaxanthenone (I). Additional evidence was furnished by infrared absorption measurements which indicated that the monosubstituent was related to 1,2,4-trisubstitution in a molecule. The position of the bromine atom was also established by another route. Metalation of 4-bromodiphenyl sulfone with *n*-butyllithium followed by carbonation gave 4-bromo-2-carboxydiphenyl sulfone.[5] Cyclization of this acid in concentrated sulfuric acid gave 2-bromo-10-thiaxanthenone-5,5-dioxide (III). This compound (III) was identical with the substance (IV) obtained by the oxidation of *x*-bromo-10-thiaxanthenone (I) with 30% hydrogen peroxide in glacial acetic acid.



Reaction of the strongly *ortho-para* directing anisole molecule with *o*-mercaptobenzoic acid gave an 80% yield of *x*-methoxy-10-thiaxanthenone.[2,6] The methoxy group was later shown to be in the 2-position by the cyclization of 2′-carboxy-4-methoxydiphenyl sulfide.[7] Cyclization of phenol with *o*-mercaptobenzoic acid gave *x*-hydroxy-10-thiaxanthenone.[8] The position of the hydroxy group in *x*-hydroxy-10-thiaxanthenone was determined by methylation and the resulting methoxy derivative was shown by Smiles and co-workers to be identical with the 2-methoxy-10-thiaxanthenone compound.[7,8]

2-Chloro-10-thiaxanthenone was prepared in a 53.4% yield by the reaction of chlorobenzene with *o*-mercaptobenzoic acid in concentrated sulfuric acid. Diazotization of 2-amino-10-thiaxanthenone followed by treatment with copper (I) chloride in hydrochloric acid yielded 2-chloro-10-thiaxanthenone and this compound was identical with that obtained from the cyclization reaction. Oxidation of 2-chloro-10-thiaxanthenone with 30% hydrogen peroxide in glacial acetic acid gave 2-chloro-10-thia-

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[1] The nomenclature and numbering are those recommended in the introduction to the 1952 Subject Index of "Chemical Abstracts."

[2] W. Prescott and S. Smiles, *J. Chem. Soc.*, 640 (1911).

[3] E. Marsden and S. Smiles, *J. Chem. Soc.*, 1353 (1911).

[4] F. Mayer, *Ber.*, **42**, 3046 (1909).

[5] W. Truce and M. Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951).

[6] S. Smiles and E. Davis, *J. Chem. Soc.*, 1290 (1910).

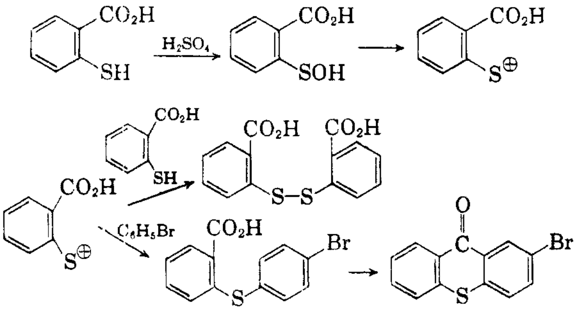
[7] K. Roberts and S. Smiles, *J. Chem. Soc.*, 863 (1929).

[8] W. Price and S. Smiles, *J. Chem. Soc.*, 3154 (1928).

xanthenone-5,5-dioxide, m.p. 226°; the literature[9] melting point is 222°.

When toluene was condensed with *o*-mercaptobenzoic acid a mixture was obtained which melted over a range of 98–110° even after repeated crystallizations. Oxidation of this mixture with 30% hydrogen peroxide in glacial acetic acid gave a 76% yield of 2-methyl-10-thiaxanthenone-5,5-dioxide[10] and a 12% yield of a second substance which might possibly be 3-methyl-10-thiaxanthenone-5,5-dioxide (V). This latter substance (V) showed 1,2,4-trisubstitution in the infrared.

The principal by-product of the *o*-mercaptobenzoic acid cyclizations is 2,2′-dithiodibenzoic acid. Stenhouse[11] has reported that disulfides could be formed by treatment of mercaptans with concentrated sulfuric acid. A possible mechanism for these *o*-mercaptobenzoic acid cyclizations in concentrated sulfuric acid is shown in the equations below. The mercapto group is oxidized[12] to the sulfenic acid[13] which immediately decomposes to the sulfenium ion.[14,15] An electrophilic attack by this sulfenium ion on bromobenzene would occur in the electron dense *para-* position. The *para* condensation is preferred over the *ortho* because of the more favorable steric conditions. The sulfenium ion could also react with *o*-mercaptobenzoic acid forming the principal by-product, 2,2′-dithiodibenzoic acid (see also ref. 11).



Christopher and Smiles[16] suggested a sulfinic acid route for these cyclizations in which a sulfoxide is formed as an intermediate and this sulfoxide was easily reduced at the expense of excess sulfinic acid to the sulfide.[17] Their conclusions were based on the ability of sulfinic acids to condense with certain aromatic compounds.[18]

EXPERIMENTAL[19]

2-Bromo-10-thiaxanthenone (I). Ten g. (0.065 mol.) of *o*-mercaptobenzoic acid was slowly added to 100 ml. of concentrated sulfuric acid and excess bromobenzene (14 ml., 0.134 mol.). The resulting tan suspension was stirred for 10 hr. then permitted to stand for an additional 10 hr. The odor of sulfur dioxide was evident during the reaction. The reaction mixture was heated on a steam bath for 1 hr., cooled, poured slowly over ice, filtered, and washed acid-free. The yellow solid was thoroughly triturated with 10% sodium hydroxide, filtered, and washed alkali-free to yield 11.5 g. (61%) of 2-bromo-10-thiaxanthenone, m.p. 161–163°. Acidification of the alkali extract gave 2.0 g. of 2,2′-dithiodibenzoic acid, m.p. 286–288°. Recrystallization of the 2-bromo-10-thiaxanthenone from a mixture of ethanol and chloroform gave a yellow solid, m.p. 166–167°. Marsden and Smiles[8] report a melting point of 141°.

Preparation of 2-bromo-10-thiaxanthenone from 2,2′-dithiodibenzoic acid, bromobenzene, and concentrated sulfuric acid gave lower yields than by the above procedure.

An infrared spectrum gave bands at 6.06μ and 12.4μ indicative of the carbonyl group and 1,2,4-trisubstitution, respectively.

2-Bromo-10-thiaxanthenone-5,5-dioxide (IV). Three g. (0.0103 mol.) of 2-bromo-10-thiaxanthenone was dissolved in 40 ml. of glacial acetic acid. To the solution was added 5 ml. of 30% hydrogen peroxide; the reaction mixture was heated to reflux and maintained, with stirring, for 4 hr. Greenish white needles separated upon cooling, which after filtration and drying weighed 2.9 g. (87.4%) and melted at 231–233°. After one crystallization from glacial acetic acid the white crystals melted at 233–234°.

Anal. Calcd. for $C_{13}H_7BrO_3S$: Br, 24.73; S, 9.92. Found: Br, 24.68, 24.82; S, 10.03, 10.11.

Infrared analysis gave a band at 8.65μ indicating the presence of the sulfone grouping in the molecule.

4-Bromo-2-carboxydiphenyl sulfone.[5] Metalation of *p*-bromodiphenyl sulfone with *n*-butyllithium, followed by carbonation and hydrolysis gave a 50% yield of 4-bromo-2-carboxydiphenyl sulfone, m.p. 153–154°, lit.[5] 153–154°.

Cyclization of 4-bromo-2-carboxydiphenyl sulfone. Using the procedure of Ullmann and Lehner,[9] 1.0 g. (0.00293 mol.) of 4-bromo-2-carboxydiphenyl sulfone was heated at 185–195° with 20 ml. of concentrated sulfuric acid. Pouring over ice gave 0.70 g. (74%) of a white solid (III), m.p. 232–234°. Admixture of III with IV showed no depression in melting point. The infrared spectra of III and IV were identical.

2-Amino-10-thiaxanthenone. 2-Nitro-10-thiaxanthenone[20] was reduced to 2-amino-10-thiaxanthenone in a 60.6% yield by the reported procedure of Mann and Turnbull,[21] m.p. 227°, lit. 227°.[4]

2-Bromo-10-thiaxanthenone (II) by diazotization of 2-amino-10-thiaxanthenone. To a stirred suspension of 3.0 g. (0.01315 mol.) of 2-amino-10-thiaxanthenone, 10 ml. of 48% hydrobromic acid and 10 ml. of water, cooled to 0°,

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(9) F. Ullmann and A. Lehner, *Ber.*, **38**, 740 (1905).

(10) W. Truce and O. Norman, *J. Am. Chem. Soc.*, **75**, 6023 (1953).

(11) J. Stenhouse, *Ann.*, **149**, 247 (1869). See also, S. Archer and C. M. Suter, *J. Am. Chem. Soc.*, **74**, 4296 (1952).

(12) The sulfurous acid produced decomposes to water and sulfur dioxide. The sharp odor of sulfur dioxide is noted during the reaction.

(13) R. Connor in H. Gilman, "Organic Chemistry," Vol. 1, John Wiley and Sons, Inc., New York, 1943, Chap. 10, p. 920, gives a discussion on the general characteristics of sulfenic acids.

(14) N. Kharasch, *J. Chem. Ed.* **33**, 585 (1956). This article contains an extensive and splendid bibliography on sulfenium ions. See also, A. J. Parker and N. Kharasch, *Chem. Revs.*, **59**, 583 (1959).

(15) R. E. Benesch and R. Benesch, *J. Am. Chem. Soc.*, **80**, 1666 (1958), and references contained therein.

(16) H. Christopher and S. Smiles, *J. Chem. Soc.*, 2046 (1911).

(17) Attempts in this laboratory to prepare 10-thiaxanthenone-5-oxide by the mild oxidation of 10-thiaxanthenone with 30% hydrogen peroxide in ethanol were unsuccessful. A possible explanation is given by A. Weizmann, *Trans. Faraday Soc.*, **36**, 978 (1940).

(18) S. Smiles and R. LeRossingnol, *J. Chem. Soc.*, 696 (1906).

(19) All melting points are uncorrected.

(20) E. Amstutz and C. Neumoyer, *J. Am. Chem. Soc.*, **69**, 1925 (1947).

(21) F. Mann and J. Turnbull, *J. Chem. Soc.*, 747 (1951).

was added a solution of 3.0 g. of sodium nitrite in 10 ml. water. The temperature of the mixture was maintained at 0–5° during the addition of the sodium nitrite solution. After a period of 10 min., 45 ml. of freshly prepared copper (I) bromide[22] solution in hydrobromic acid was added to the mixture. A vigorous reaction followed the addition of the catalyst, and the red diazotized mixture became brown. The mixture was subsequently heated on the steam-bath for 30 min. and allowed to cool. The supernatant liquid was decanted off, and the brown residue was treated with hydrobromic acid and washed with water.

The crude black material was dissolved in benzene and the solution was chromatographed on an alumina column using benzene as the eluent. From the eluate was obtained 2.0 g. (52.4%) of crude 2-bromo-10-thiaxanthenone melting at 163–167°. Crystallization from ethanol gave 1.0 g. (26.2%) of pure product melting at 166–167°. A mixture melting point of this material (II) with I showed no depression. Oxidation of 2-bromo-10-thiaxanthenone (II) with 30% hydrogen peroxide in glacial acetic acid gave 2-bromo-10-thiaxanthenone-5,5-dioxide which showed no depression in melting point when admixed with either III or IV.

2-Chloro-10-thiaxanthenone. Treatment of 10 g. (0.0648 mol.) of *o*-mercaptobenzoic acid with excess chlorobenzene and concentrated sulfuric acid in an analogous manner as that described for the preparation of 2-bromo-10-thiaxanthenone (I) gave 8.6 g. (53.4%) of yellow solid melting at 152–153°.

Anal. Calcd. for $C_{13}H_7ClOS$: C, 63.30; H, 2.86. Found: C, 63.35, 63.41; H, 3.08, 3.15.

The infrared spectrum showed absorption bands at 6.06μ, 12.4μ, and 13.4μ, characteristic of the carbonyl, 1,2,4-trisubstitution and 1,2-disubstitution, respectively.

A Sandmeyer reaction on 2-amino-10-thiaxanthenone gave a 46% yield of 2-chloro-10-thiaxanthenone, m.p. 150–151.5°, which was identical with the *x*-chloro-10-thiaxanthenone obtained by the cyclization of *o*-mercaptobenzoic acid with chlorobenzene. Oxidation of 2-chloro-10-thiaxanthenone with 30% hydrogen peroxide in glacial acetic acid gave an 85% yield of 2-chloro-10-thiaxanthenone-5,5-dioxide, m.p. 226°. Ullmann and Lehner[9] prepared 2-chloro-10-thiaxanthenone-5,5-dioxide by cyclization of 4′-chloro-2-carboxydiphenyl sulfone and reported a melting point of 222°.

x-Methyl-10-thiaxanthenone. Reaction of toluene with *o*-mercaptobenzoic acid in a manner described for 2-bromo-10-thiaxanthenone (I) gave 7.9 g. (53%) of yellow solid melting 98–110°. Several crystallizations did not improve the melting point. Smiles and Davis[6] reported a melting point of 96–97° to the product they isolated from the reaction of *o*-mercaptobenzoic acid and toluene. 2-Methyl-10-thiaxanthenone[23] has a melting point of 123°.

An infrared analysis of the isomeric mixture showed absorption bands at 6.06μ, 12.4μ, and 13.4μ, characteristic of the carbonyl, 1,2,4-trisubstitution and 1,2-disubstitution, respectively.

2-Methyl-10-thiaxanthenone-5,5-dioxide and 3-methyl-10-thiaxanthenone-5,5-dioxide. Three and seven-tenths g. (0.0164 mol.) of *x*-methyl-10-thiaxanthenone was dissolved in 25 ml. of glacial acetic acid. To the solution was added 5 ml. of 30% hydrogen peroxide and the reaction mixture heated to reflux and maintained, with stirring for 4 hr. Pouring over ice gave 4.0 g. (94.7%) of yellow crystals melting at 158–190°. Fractional crystallization from ethanol gave 3.2 g. (76%) of 2-methyl-10-thiaxanthenone-5,5-dioxide,[10] m.p. 199°, lit. 199°, and 0.5 g. (12%) of yellow powder (V), m.p. 158.5–160°. The latter substance (V) gave absorption bands at 6.06μ, 12.4μ, and 13.4μ in the infrared which are characteristic of the carbonyl, 1,2,4-trisubstitution and 1,2-disubstitution, respectively.

Anal. Calcd. for $C_{14}H_{10}O_3S$: S, 12.38. Found: S, 12.33, 12.46.

Compound V could possibly be 3-methyl-10-thiaxanthenone-5,5-dioxide since the infrared did give absorption indicative of 1,2,4-trisubstitution and no absorption for 1,2,3-trisubstitution.

Acknowledgment. Infrared spectra were obtained through the courtesy of the Institute for Atomic Research, Iowa State College.

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[22] A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 2nd ed., 1951, p. 186.

[23] F. Mayer, *Ber.*, **43**, 584 (1910).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE R. J. REYNOLDS TOBACCO CO.]

Composition of Cigarette Smoke. III. Phytadienes

ALAN RODGMAN

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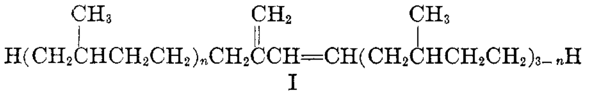
A series of isomeric conjugated phytadienes has been isolated from the cigarette smoke of a cased commercial blend of tobaccos. Evidence is presented to indicate that this series contains 3-methylene-7,11,15-trimethyl-1-hexadecene (neophytadiene), 3,7,11,15-tetramethyl-1,3-hexadecadiene, 2,6,10,14-tetramethyl-1,3-hexadecadiene, and a 1,2,4-trialkyl-1,3-butadiene and possibly as many as nine other conjugated phytadienes. Neophytadiene was the only phytadiene actually separated from the mixture. A similar series of phytadienes was observed in the cigarette smoke from flue-cured, burley, Turkish, and four other different commercial blends of tobacco.

The diterpene neophytadiene (I, *n* = 3) has



$$H(CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2)_nCH_2\overset{\overset{CH_2}{\|}}{C}CH{=}CH(CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2)_{3-n}H$$

I

been identified as a component of flue-cured tobacco by Rowland,[1] as a component of aged burley and flue-cured tobaccos and as a major component of the total volatile oils of aged burley and flue-cured tobaccos by Gladding *et al.*,[2a,2b] as a component of

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[1] R. L. Rowland, *J. Am. Chem. Soc.*, **79**, 5007 (1957).

[2] (a) R. N. Gladding, W. B. Wartman, and H. E. Wright, Paper presented at the 11th Annual Tobacco Chemists' Research Conference, New Haven, Conn., Oct. 10–11, 1957. (b) R. N. Gladding, W. B. Wartman, and H. E. Wright, *J. Org. Chem.*, **24**, 1359 (1959).