[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

# Derivatives of Sulfenic Acids. IV. The Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Aromatic Systems[1]

BY CHARLES M. BUESS[2] AND NORMAN KHARASCH

In the course of studies to establish the existence of the 2,4-dinitrobenzenesulfenium ion, $(NO_2)_2C_6H_3S^+$, in the bright-red solutions of 2,4-dinitrobenzenesulfenyl chloride in sulfuric acid,[3] it was found that these solutions were decolorized by the addition of benzene, and that phenyl 2,4-dinitrophenyl sulfide could be isolated from the reaction mixtures. This suggested that reagents which would promote the ionic dissociation of the sulfenyl chloride would also facilitate the substitution of the 2,4-dinitrophenylthio radical into systems which would not normally be susceptible to attack by the sulfenyl chloride alone. As a first step in the study of this type of reaction, it was decided to attempt to extend the analytical utility of 2,4-dinitrobenzenesulfenyl chloride to the characterization of various aromatic systems. The suitability of this reagent for the identification of amines[4] and olefins[5] has been demonstrated previously.

The reaction of 1-anthraquinonesulfenyl chloride with benzene in the presence of aluminum chloride, yielding 1-anthraquinonyl phenyl sulfide, has been described,[6] but attempts to extend the reaction to benzenesulfenyl chloride and *p*-toluenesulfenyl chloride were unsuccessful.[7] Under similar conditions the product of the reaction of trichloromethanesulfenyl chloride with benzene, in the presence of rather large proportions of aluminum chloride, was reported to be thiobenzophenone.[8] In the present study, however, it was found that aluminum chloride effects smooth reactions between 2,4-dinitrobenzenesulfenyl chloride and various aromatic hydrocarbons, as well as their halogenated derivatives, yielding aryl 2,4-dinitrophenyl sulfides. These reactions are of the Friedel–Crafts type, the sulfenyl chloride playing a role similar to that taken by an alkyl halide in the regular Friedel–Crafts alkylations. As in the standard Friedel–Crafts reactions, aluminum chloride catalysis was not satisfactory in the case of thiophene. 2-Thienyl 2′,4′-dinitrophenyl sulfide was readily prepared, however, through the use of stannic chloride catalysis. With active aromatic nuclei, such as resorcinol and dimethylaniline, the corresponding 2,4-dinitrophenyl sulfides may be obtained without resort to the use of catalysts. The aryl 2,4-dinitrophenyl sulfides obtained in the present study are listed in Table I.

The general procedure for obtaining aryl 2,4-dinitrophenyl sulfides from aromatic hydrocarbons and their halogenated derivatives is given in the experimental section. The use of a high ratio of aluminum chloride to sulfenyl chloride is recommended to ensure rapid completion of reaction. The thioarylation does proceed with smaller amounts of aluminum chloride; but, under the prescribed conditions, the desired products are not as readily purified and are obtained in lower yields. Whenever possible, the reactions are best carried out at low temperatures, because this practically eliminates the formation of dark-colored side products.

The aryl 2,4-dinitrophenyl sulfides are readily purified by crystallization from absolute ethyl alcohol or mixtures of alcohol and benzene. Excellent samples were obtained after one or two crystallizations, even in those cases in which the products might be expected to consist of two or more isomeric sulfides.

Bost and co-workers[9,10] have previously prepared each of the isomeric tolyl 2,4-dinitrophenyl sulfides and sulfones, by methods involving reactions of thiocresols and 2,4-dinitrochlorobenzene. It was therefore a simple matter to establish conclusively that the product obtained from the sulfenyl chloride and toluene was *p*-tolyl 2,4-dinitrophenyl sulfide. From the latter, by vigorous oxidation, there was obtained an authentic sample of the previously unreported 4-carboxyphenyl 2′,4′-dinitrophenyl sulfone. This compound was found to have a melting value of 272–274°, which was substantially different from that of the known 2-carboxyphenyl 2′,4′-dinitrophenyl sulfone[11] (m. p. 215–217°), as well as the 3-carboxyphenyl 2′,4′-dinitrophenyl sulfone (m. p. 226–227°) which we prepared for purposes of comparison. Each of the derivatives (listed in Table I) from ethylbenzene, isobutylbenzene, *s*-butylbenzene and bibenzyl, on oxidation, yielded 4-carboxyphenyl 2′,4′-dinitrophenyl sulfone. This established that these derivatives, as also in the case of toluene, were the para isomers.

The *t*-butylphenyl 2,4-dinitrophenyl sulfide, obtained from *t*-butylbenzene and 2,4-dinitrobenzenesulfenyl chloride, could not be converted by

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[1] Presented before the Organic Division of the American Chemical Society, Atlantic City, New Jersey, September, 1949.

[2] Abbott Laboratories Research Fellow, University of Southern California, 1947–1949.

[3] Evidence for the dissociation, in accord with the equation, $(NO_2)_2C_6H_3SCl + H_2SO_4 \rightleftarrows (NO_2)_2C_6H_3S^+ + HCl + HSO_4^-$ was reported by us, in part, at the San Francisco meeting of the American Chemical Society, April, 1949, and will be presented in a following paper.

[4] Billman, Garrison, Anderson and Wolnak, THIS JOURNAL, **63**, 1920 (1941).

[5] Kharasch and Buess, *ibid.*, **71**, 2724 (1949).

[6] Fries and Schurmann, *Ber.*, **52**, 2170 (1919).

[7] Lecher, *et al.*, *ibid.*, **58**, 409 (1925).

[8] Vorlander and Mittag, *ibid.*, **52**, 418 (1919); *cf.* also Connolly and Dyson, *J. Chem. Soc.*, 822 (1934).

[9] Bost, Turner and Norton, THIS JOURNAL, **54**, 1985 (1932).

[10] Bost, Turner and Conn, *ibid.*, **55**, 4956 (1933).

[11] Mayer, *Ber.*, **43**, 593 (1910).

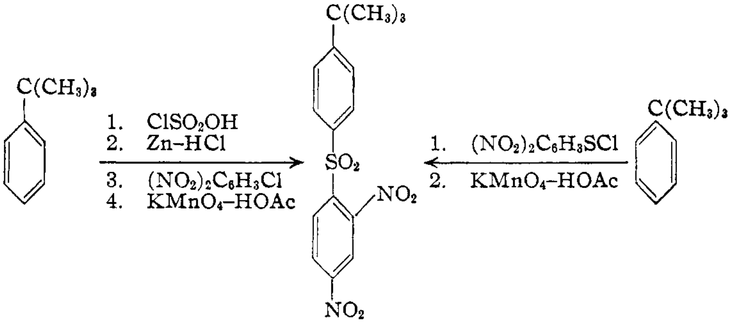
TABLE I

DERIVATIVES OF AROMATIC COMPOUNDS WITH 2,4-DINITROBENZENESULFENYL CHLORIDE

| Aromatic compd. | Aryl 2,4-dinitrophenyl sulfide M. p., °C.[a] | Yield, %[b] | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|
| Benzene | 120–120.5 | 75 | $C_{12}H_8N_2O_4S$[c] | | | | |
| Toluene | 102–103 | 85 | $C_{13}H_{10}N_2O_4S$[c] | | | | |
| *p*-Xylene | 134–135 | 85 | $C_{14}H_{12}N_2O_4S$ | 55.25 | 55.54 | 3.98 | 4.21 |
| Ethylbenzene | 97–97.5 | 90 | $C_{14}H_{12}N_2O_4S$ | 55.25 | 55.46 | 3.98 | 4.19 |
| *n*-Butylbenzene | 72.5–73.5 | 75 | $C_{16}H_{16}N_2O_4S$ | 57.82 | 58.04 | 4.85 | 4.90 |
| Isobutylbenzene | 99–100 | 85 | $C_{16}H_{16}N_2O_4S$ | 57.82 | 57.91 | 4.85 | 4.89 |
| *s*-Butylbenzene | 88–89 | 70 | $C_{16}H_{16}N_2O_4S$ | 57.82 | 58.00 | 4.85 | 5.02 |
| *t*-Butylbenzene | 130–131 | 50 | $C_{16}H_{16}N_2O_4S$ | 57.82 | 57.91 | 4.85 | 4.99 |
| *p*-Di-*t*-butylbenzene | 150–151 | 50 | $C_{20}H_{24}N_2O_4S$ | 61.83 | 61.92 | 6.23 | 6.37 |
| Biphenyl | 142–143 | 90 | $C_{18}H_{12}N_2O_4S$[c] | | | | |
| Bibenzyl | 131.5–133 | 40 | $C_{20}H_{16}N_2O_4S$ | 63.14 | 63.38 | 4.24 | 4.42 |
| Naphthalene | 173–174 | 90 | $C_{16}H_{10}N_2O_4S$[d] | | | | |
| Phenanthrene | 250–251 | 65 | $C_{20}H_{12}N_2O_4S$ | 63.82 | 63.63 | 3.21 | 3.32 |
| Chlorobenzene | 123–124 | 70 | $C_{12}H_7ClN_2O_4S$[d] | | | | |
| Bromobenzene | 140–141 | 70 | $C_{12}H_7BrN_2O_4S$[d] | | | | |
| Thiophene | 119–119.5 | 70 | $C_{10}H_6N_2O_4S_2$[c] | | | | |
| Resorcinol | 183–184 | 91 | $C_{12}H_8N_2O_6S$ | 46.75 | 46.84 | 2.61 | 2.60 |
| N,N-Dimethylaniline | 175–176 | 85 | $C_{14}H_{13}N_3O_4S$ | 52.65 | 52.80 | 4.10 | 3.93 |

[a] All melting points reported in this paper are uncorrected. [b] The yields were calculated on the crude products. Except in the case of the product from phenanthrene, the crude products melted within 10° of the purified samples. The crude product from phenanthrene melted at 228–231°. [c] Bost, Turner and Norton[9] reported m. p.'s of the following 2,4-dinitrophenyl sulfides: phenyl, 121°; *p*-tolyl, 103°; biphenyl, 146°; thienyl, 119°. [d] Bost, Turner and Conn,[10] reported the melting points of the following 2,4-dinitrophenyl sulfides: 1-naphthyl, 176°; 2-naphthyl, 145°; *p*-chlorophenyl, 123°; *p*-bromophenyl, 142°.

oxidation to a carboxyphenyl sulfone—as was done for the other butylbenzene derivatives described above. The *t*-butylphenyl sulfide was, however, shown to be the para isomer by an independent synthesis of *p*-*t*-butylphenyl 2,4-dinitrophenyl sulfone, which proved to be identical with the sulfone obtained by oxidation of the sulfide prepared *via* the sulfenyl chloride.



By reaction sequences involving aromatic thiols of known structures, similar to the one illustrated for *t*-butylbenzene above, the derivatives from chlorobenzene, bromobenzene and biphenyl were shown to be the para isomers; and the derivative from thiophene was proved to be the 2-thienyl isomer. Both of the naphthyl 2,4-dinitrophenyl sulfides are known.[10] The sulfide obtained by means of the sulfenyl chloride corresponds to the 1-naphthyl sulfide. Although the structures for the derivatives from dimethylaniline and resorcinol were not confirmed by independent means in this study, there can be little doubt that these products are, respectively, 4-dimethylaminophenyl 2′,4′-dinitrophenyl sulfide and 2,4-dihydroxyphenyl 2′,4′-dinitrophenyl sulfide.

The excellent yields of products obtained in the reactions, and the high selectivity which the reagent, 2,4-dinitrobenzenesulfenyl chloride, displays in differentiating closely related aromatic systems suggest that the method described in this paper promises to become a most valuable procedure for the characterization of aromatic substances.

## Experimental

**Starting Materials.**—2,4-Dinitrobenzenesulfenyl chloride was prepared by the catalytic chlorinolysis of 2,4-dinitrophenyl disulfide.[12] Reagent-grade samples of the commercially available aromatic compounds were employed in the preparation of analytical samples, but satisfactory products were also obtained from technical grade samples of some compounds. *n*-Butylbenzene[13] and isobutylbenzene[14] were prepared by the hydrogenation of 4-phenyl-1-butene and 2-methyl-3-phenylpropene, respectively. *s*-Butylbenzene,[15a] *t*-butylbenzene[15b] and *p*-di-*t*-butylbenzene[15b] were prepared by modified Friedel-Crafts reactions.

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(12) Kharasch, Gleason and Buess, THIS JOURNAL, **72**, 1796 (1950). Since 2,4-dinitrobenzenesulfenyl chloride is known to be explosive when heated to elevated temperatures, particular caution must be taken to avoid indiscriminate heating of this sulfenyl chloride above 90–100°.

(13) Karabinos and Lamberti, Natl. Advisory Comm. Aeronautics, Tech. Note No. 1019 (1946).

(14) Buess, Karabinos, Kunz and Gibbons, *ibid.*, Tech. Note No. 1021 (1946).

(15) (a) Huston and Kaye, THIS JOURNAL, **64**, 1576 (1942); (b) Huston, Fox and Binder, *J. Org. Chem.*, **3**, 251 (1938).

**General Procedure for the Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Aromatic Compounds in the Presence of Aluminum Chloride.**—With the exceptions noted below, all derivatives listed in Table I were prepared by this general procedure.

Ethylene chloride of adequate purity is obtained by distilling the commercial product until the distillate is clear, and discarding the forerun. A solution containing 1.00 g. of 2,4-dinitrobenzenesulfenyl chloride in 15 ml. of this solvent is cooled to 5° in an ice-bath. Approximately 1 g. of anhydrous aluminum chloride is then added and the mixture is shaken for one minute. To the resulting red mixture is then added 1.5-2.0 g. of the aromatic compound. If a solid, the aromatic compound is dissolved in the minimum quantity of ethylene chloride prior to addition. The temperature rises spontaneously and hydrogen chloride is evolved. The flask is rotated for one to two minutes in the ice-bath. Five milliliters of ethyl alcohol is then added slowly so that the temperature does not exceed 30°. If the temperature of the reaction mixture is not controlled, the overheating promotes the formation of a dark mixture from which the isolation of the desired sulfide is realized only with difficulty. With proper temperature control, addition of the alcohol generally turns the reaction mixture to a transparent yellow or reddish-brown solution. The solution is then washed twice with water or dilute hydrochloric acid to remove the aluminum compounds. The layer containing the organic product is then concentrated to approximately 5 ml. in an air stream or by distillation of the solvent, and to the resulting solution there is then added an equal volume of absolute ethyl alcohol. The desired sulfide generally separates from this solution on cooling, but in a few cases the ethylene chloride must be completely replaced by ethyl alcohol to obtain a satisfactory yield. The sulfides may then be recrystallized from absolute ethyl alcohol, or, if the derivatives have relatively high melting points, alcohol-benzene mixtures may be used to advantage.

In preparing analytical samples of the new sulfides listed in Table I, the products were rigorously purified by adsorption of traces of impurities on a column of activated alumina, using benzene solutions. The 2,4-dinitrophenyl sulfides were completely eluted with excess benzene, whereas a dark residual band was not. Presumably, the colored impurities are those which are typical of Friedel-Crafts reactions. The chromatographic purification is not, however, considered essential for characterization purposes.

**Benzene, Chlorobenzene, Bromobenzene and Phenanthrene.**—The reactions of these compounds with 2,4-dinitrobenzenesulfenyl chloride were carried out exactly as described above, except that a temperature of 20° was employed.

**Thiophene.**—Stannic chloride was prepared by shaking metallic tin with a solution of chlorine in ethylene chloride. The excess chlorine was removed by distillation of a fraction of the solvent at reduced pressure. A solution of stannic chloride resulting from the reaction of 1.5 g. of tin with excess chlorine in 15 ml. of ethylene chloride was mixed with a solution of 1.0 g. of 2,4-dinitrobenzenesulfenyl chloride in 15 ml. of ethylene chloride. The resulting solution was yellow, not red as in the case with aluminum chloride. Three milliliters of thiophene was then added, and the resulting solution was refluxed for one-half hour. Hydrogen chloride was evolved. After cooling, the reaction mixture was treated as in the general procedure, leading to 2-thienyl 2′,4′-dinitrophenyl sulfide, m.p. 119-119.5°.

**Resorcinol.**—A solution of 2.00 g. of resorcinol and 0.50 g. of 2,4-dinitrobenzenesulfenyl chloride in 5 ml. of glacial acetic acid was refluxed for two minutes. The solution was cooled, diluted to 200 ml. with water, and allowed to stand overnight. Orange crystals (0.60 g., m.p. 180-181°) separated. Recrystallization from benzene gave a product of higher melting point, 183-184°.

**Dimethylaniline.**—A solution of 1 ml. of dimethylaniline and 0.15 g. of 2,4-dinitrobenzenesulfenyl chloride in 15 ml. of anhydrous ethyl ether was refluxed for ten minutes. The solution turned brown and dimethylanilinium chloride separated. Fifty ml. of water was added and the ether and excess dimethylaniline were co-distilled with part of the water. The red solid residue was separated from the remaining solvent, washed with hot absolute ethyl alcohol, and the crude product (0.17 g., m.p. 173-174°) was recrystallized from benzene. In this way, the melting range was raised to 175-176°.

***p*-Tolyl 2,4-Dinitrophenyl Sulfone.**—This substance, m.p. 187-188°, resulted on oxidation of the derivative from toluene with potassium permanganate in acetic acid.[9]

**4-Carboxyphenyl 2′,4′-Dinitrophenyl Sulfone.**—This compound (m.p. 272-274°) was obtained in 60% yield from the derivative of toluene by oxidation with chromic acid.[16]

*Anal.* Calcd. for $C_{13}H_8N_2O_8S$: C, 44.32; H, 2.29. Found: C, 44.71; H, 2.57.

Oxidation of the other derivatives from monoalkylbenzenes, except the one from *t*-butylbenzene, similarly produced 4-carboxyphenyl 2′,4′-dinitrophenyl sulfone, m.p. 272-274°.

**3-Carboxyphenyl 2′,4′-Dinitrophenyl Sulfone.**—A sample of this compound was prepared so that its properties might be compared with those of 4-carboxyphenyl 2′,4′-dinitrophenyl sulfone. 3-Mercaptobenzoic acid was prepared according to the procedure of Smiles and Stewart.[17] The latter product (0.15 g.) was dissolved in 0.40 ml. of 10% sodium hydroxide solution, and this solution was diluted with 10 ml. of absolute ethyl alcohol. 2,4-Dinitrochlorobenzene (0.20 g.) in 10 ml. of absolute ethyl alcohol was added, and the resulting mixture was refluxed for five minutes, then poured into 100 ml. of water. After being allowed to stand for several hours, the organic material was collected on the filter plate. The product, after two recrystallizations from benzene, melted at 193-194°; yield 0.22 g. (71%).

*Anal.* Calcd. for $C_{13}H_8N_2O_6S$: C, 48.75; H, 2.52. Found: C, 48.98; H, 2.52.

3-Carboxyphenyl 2′,4′-dinitrophenyl sulfone was prepared from the above sulfide by oxidation with chromic acid.[16] This compound was obtained in 68% yield and was found to melt at 226-227°.

*Anal.* Calcd. for $C_{13}H_8N_2O_8S$: neut. equiv., 352.3. Found: neut. equiv., 349.

**Alternate Syntheses of Certain 2,4-Dinitrophenyl Sulfides and Sulfones.**—Samples of 4-chloro-,[18] 4-bromo-[18] and 4-*t*-butylbenzenesulfonyl[19] chlorides and 2-thiophenesulfonyl chloride[20] were prepared by treatment of the appropriate aromatic compound with chlorosulfonic acid. 4-Biphenylsulfonyl chloride was obtained by treatment of the potassium salt of the corresponding sulfonic acid[21] with phosphorus pentachloride. These sulfonyl chlorides were then reduced to the corresponding mercaptans with zinc and alcoholic hydrochloric acid. Treatment of the mercaptans with equivalent quantities of sodium hydroxide and 2,4-dinitrochlorobenzene in ethyl alcohol yielded the following 2,4-dinitrophenyl sulfides: 4-chlorophenyl, m.p. 123-124°; 4-bromophenyl, 140-141°; 4-*t*-butylphenyl, 130-131°; 2-thienyl, 118-119°; and 4-biphenylyl, 142-143°. The melting points of samples of these sulfides were not lowered by the addition of samples of the corresponding derivatives from chlorobenzene, bromobenzene, *t*-butylbenzene, thiophene and biphenyl obtained *via* 2,4-dinitrobenzenesulfenyl chloride. As a further check, samples of both sets of the sulfide products, listed above, were oxidized to the corresponding sulfones with potassium permanganate in acetic acid. The melting points of the corresponding aryl 2,4-dinitrophenyl sulfones, whether ob-

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[16] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 198.

[17] Smiles and Stewart, *J. Chem. Soc.*, 1795 (1921).

[18] Huntress and Carten, THIS JOURNAL, **62**, 511 (1940).

[19] Huntress and Autenrieth, *ibid.*, **63**, 3446 (1941).

[20] Steinkopf and Hopner, *Ann.*, **501**, 174 (1933).

[21] Latschinow, *Ber.*, **6**, 193 (1873).

tained *via* the sulfonyl chlorides or from the reaction of 2,4-dinitrobenzenesulfenyl chloride, were: 4-chlorophenyl, 168–169°; 4-bromophenyl, 189–190°; 4-*t*-butylphenyl, 128–129°; 2-thienyl, 142–143°; and 4-biphenylyl, 169–170°. These melting points are in agreement with the values obtained by Bost, Turner and Norton[9] and Bost, Turner and Conn.[10] In no case was the melting point of a sulfone obtained from a sulfonyl chloride lowered by the addition of the sulfone with the same molecular formula obtained using 2,4-dinitrobenzenesulfenyl chloride. Biphenylyl 2,4-dinitrophenyl sulfone is yellow; the other sulfones reported above are nearly colorless. 4-*t*-Butylphenyl 2',4'-dinitrophenyl sulfone, which is apparently new, was also obtained by oxidation of the derivative from *t*-butylbenzene with chromic acid.

*Anal.* Calcd. for $C_{16}H_{16}N_2O_6S$: C, 52.74; H, 4.43. Found: C, 52.76; H, 4.68.

**Acknowledgment.**—The authors wish to express appreciation to the Abbott Laboratories of North Chicago, Illinois, for a fellowship grant in support of this work. The microanalyses for carbon and hydrogen were carried out by the late Dr. Gertrud Oppenheimer and by G. Swinehart of the California Institute of Technology.

## Summary

2,4-Dinitrobenzenesulfenyl chloride has been found to undergo a Friedel–Crafts type reaction with a variety of aromatic compounds.

The 2,4-dinitrophenylthio group has been shown to enter the 4-position of several monoalkyl- and monohalobenzenes, the 1-position of naphthalene, and the 2-position of thiophene.

The reaction offers an excellent method for the characterization of aromatic compounds.

LOS ANGELES, CALIF. RECEIVED FEBRUARY 13, 1950

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[CONTRIBUTION FROM THE DIVISION OF BIOCHEMISTRY, UNIVERSITY OF CALIFORNIA MEDICAL SCHOOL]

# Pteridine Studies. I. Mercaptopteridines

BY EMERY M. GAL[1]

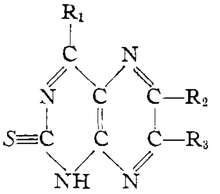
The observations on tumor-growth influencing properties of folic acid analogs and some pteridines[2] led us to undertake the synthesis and biological assay of a series of known and of hitherto unrecorded pteridines. The results obtained with 2,4-diaminopteridine,[3,4] and with 4-aminopteroylglutamic acid[5] led to a more extensive study of the 4-amino substituted pteridine ring. It was of interest to note how the mercapto group in the 2 position influenced this activity.

Synthesis of 2-mercapto-4,6,7-trihydroxypyrimido(4,5-b)pyrazine was reported by Elion and Hitchings,[6] 4-hydroxy-2-mercaptopyrimido(4,5-b)pyrazine by Polonovski, Vieillefosse and Pesson[7] and the 4-amino-6,7-dihydroxy-2-mercaptopyrimido(4,5-b)pyrazine by Wieland and Liebig.[8] These syntheses were repeated and confirmed.

The method of synthesis is based on the condensation of 2-mercapto-4,5,6-triaminopyrimidine and of the 4,5-diamino-6-hydroxy-2-mercaptopyrimidine with dicarbonyl reagents such as diacetyl, glyoxal, pyruvic acid and oxalic acid. The condensation with pyruvic acid led to the formation of isomers.[6] This was now confirmed with mer-

TABLE I

THE 2-MERCAPTOPTERIDINE RING



| Compound | R₁ | R₂ | R₃ | U. V. spectra in 0.1 *N* NaOH Max. Å. | min. *p*H 8.55–9.0 | Soly. in phosphate buffer at *p*H 7.4 mg./100 ml. |
|---|---|---|---|---|---|---|
| I | $NH_2$ | .. | 3870<br>.. | 3300<br>2930 | 2650 | 5 |
| II | $NH_2$ | OH | OH | 3150 shoulder<br>2700 | 2460 | 125 (8) |
| III | $NH_2$ | $CH_3$ | OH | 3570<br>2675 | 3100<br>2525 | 25 |
| IV | $NH_2$ | OH | $CH_3$ | 3545<br>3025 | 3325<br>2790 | 110 |
| V | $NH_2$ | $CH_3$ | $CH_3$ | 3920<br>3115 | 3495<br>2890 | 3 |
| VI | OH | .. | .. | 3750<br>2870 | 3300<br>2620 | 250 (7) |
| VII | OH | OH | OH | 3180<br>2520 | 2800<br>2320 | 125 (6 |
| VIII | OH | OH | $CH_3$ | 3525<br>3020<br>2515 | 3325<br>2700<br>2400 | 80 |
| IX | OH | $CH_3$ | OH | 3420<br>3015<br>2545 | 3325<br>2750<br>2425 | 120 |
| X | OH | $CH_3$ | $CH_3$ | 3850<br>3020 | 3350<br>2690 | 45 |
| Pyrimidines: | | | | | | |
| (a) 4,5-Diamino-6-hydroxy-2-mercapto | | | | 2725 | 2455 | |
| (b) 2-Mercapto-4,5,6-triamino | | | | 2640<br>2350 shoulder | 2580 | |

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[1] U. S. Public Health Special Fellow. This work was supported by a grant from the Cancer Research Grants Branch, U. S. Public Health Service, to D. M. Greenberg.

[2] (a) Lewissohn, Leuchtenberger and Leuchtenberger, *Proc. Soc. Exp. Biol. and Med.*, **56**, 144 (1944); (b) Thiersch and Philips, *Am. J. Med. Sci.*, **217**, 575 (1949).

[3] LaDu, Fineberg, Gal and Greenberg, *Proc. Soc. Exper. Biol. and Med.*, in press (also Abst. 115th National Meeting of A. C. S., San Francisco, March, 1949).

[4] Thiersch and Stock, *Cancer*, **2**, 863 (1949).

[5] Olson, Hutchings and SubbaRow, *J. Biol. Chem.*, **175**, 359 (1948).

[6] Elion and Hitchings, THIS JOURNAL, **26**, 2553 (1947).

[7] Polonovski, Viellefosse and Pesson, *Bull. soc. chim.*, [5] **12**, 78 (1945).

[8] Wieland and Liebig, *Ann.*, **555**, 150 (1944).