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ultraviolet absorption spectra of cholestenone and cholesterilene has been made by Cox and Spencer (4) in a consideration of the molecular structure of enol esters of cholestenone.)

BECK, S., KIRBY, A. H. M., and PEACOCK, P. R. Cancer Research, 5: 135. 1935. BURCHARD, H. Chem. Zentr. 61(1): 25. 1890. Cox, R. H. and SPENCER, E. Y. Can. J. Chem. 29: 217. 1951. Cox, R. H. and SPENCER, E. Y. Can. J. Chem. 29: 398. 1951. DELS, O. and ABDERHALDEN, E. BET. 37: 3099. 1904.

2

3. 4.

5.

DIELS, O., GADKE, W., and KORDING, P. AM DIELS, O. and LINN, K. Ber. 41: 260. 1908. FANTL, P. Monatsh. 47: 251. 1926. 1927 6. Ann. 459: 21.

8

9 Halasz, A. Ann. Chim. 14: 318. 1940.

9. HALASZ, A. Ann. Chim. 14: 318. 1940.
10. HEIBRON, I. M. and SEXTON, W. A. J. Chem. Soc. 347. 1928.
11. LIEBERMANN, C. Ber. 18: 1803. 1885.
12. MARKER, R. E., WITLE, E. L., and NIXON, L. W. J. Am. Chem. Soc. 59: 1369. 1937.
13. OPPENAUER, R. V. Org. Syntheses, 21: 18. 1941.
14. PEACOCK, P. R. and KIRBY, A. H. M. Cancer Research, 4: 94. 1944.
15. SPENCER, E. Y. and COX, R. H. Unpublished data.
16. STRAIN, W. H. Treatise of organic chemistry. *Edited by* GILMAN, H. 2nd ed. John Wiley and Sons, New York. 1943. p. 1341.
17. VELDSTRA, H. Nature, 144: 246. 1939.

RECEIVED APRIL 16, 1951. FACULTY OF PHARMACY, R. G. LINBURG UNIVERSITY OF BRITISH COLUMBIA, R. H. Cox E. Y. SPENCER. VANCOUVER, B.C. AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SASKATCHEWAN, SASKATOON, SASK.

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### Aryldiguanidines\*

Some aryldiguanidines were prepared by treating aryldiamines with cyanamide. These are described below in the experimental section. ·...

#### EXPERIMENTAL\*\*

### Tolyl-2,5-diguanidine

Fifteen grams (0.077 mole) of 2,5-diaminotoluene dihydrochloride and 7.3 gm. (0.174 mole) of cyanamide were covered with 35 cc. of absolute alcohol. Dry, oxygen-free nitrogen was bubbled through the reaction mixture while it was heated on a steam bath for eight hours. After the reaction mixture had cooled in the refrigerator, the solid was removed by filtration and washed with ethanol. The purplish-white solid melted at 283°-295°C. with decomp., yield 18.09 gm. (84.3%). Two crystallizations from 95% ethanol raised the melting point of the 2,5-diguanidinotoluene dihydrochloride to 294°-295°C. with decomp. This dihydrochloride was previously reported (1) as melting at 290°-292°C. with decomp.

\* Issued as DRCL Report No. 64.

\*\* All melting points were determined on a Kofler block and are corrected.

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# Anal.\*\*\* Calc. for C<sub>9</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>6</sub>: C, 38.80; H, 5.74; N, 30.11. Found: C, 38.90; H, 5.67; N, 29.88.

An aqueous solution of 1 gm. of tolyl-2,5-diguanidine dihydrochloride on treatment with a saturated aqueous picric acid solution gave 1.96 gm. (82.4%) of a yellow picrate melting at 170°-175°C. One crystallization from water raised the melting point to a constant value of 177.5°-177.9°C., vield 1.72 gm.

Anal. Calc. for  $C_{21}H_{20}N_{12}O_{14}$ : C, 38.00; H, 3.03; N, 25.30. Found: C, 37.96; H, 3.50; N, 25.15.

# Tolyl-3,4-diguanidine

3,4-Diaminotoluene dihydrochloride (15 gm., 0.077 mole) and 7.3 gm. (0.174 mole) of cyanamide in 35 cc. of absolute alcohol were heated as above for three hours. No solid was obtained on cooling the solution to 4°. A black, tarry residue remained after the alcohol was removed *in vacuo* under nitrogen. The tar was dissolved in 100 cc. of water and the solution almost saturated with potassium carbonate. The solution was allowed to stand at 4° several hours after which the tolyl-3,4-diguanidinium carbonate (17.55 gm.; 85.0%) was removed by filtration. The crude carbonate melted with decomposition at 101°-104°C. with shrinkage at 95°. This melting point could not be improved by crystallization, therefore a sample (1.12 gm.) was dissolved in water and converted to the picrate in the usual manner. One crystallization from water gave 1.32 gm. (47.7%) of a yellow crystalline picrate melting at 238.5°-239.5°C.

Anal. Calc. for  $C_{21}H_{20}N_{12}O_{14}$ : C, 38.00; H, 3.03; N, 25.30. Found: C, 38.20; H, 3.11; N, 25.11.

## Anisyl-2,4-diguanidine

Cyanamide (7.56 gm., 0.18 mole) and 15 gm. (0.071 mole) of 2,4-diaminoanisole dihydrochloride in 32 cc. of absolute ethanol were treated in the same manner as described above for the preparation of 3,4-diguanidinotoluene. The carbonate was obtained in 25.8% (5.2 gm.) yield. It melted over a range of  $165^{\circ}-170^{\circ}$ C. with decomp. A 250 mgm. portion of this product gave 512 mgm. (85.4%) of a crystalline picrate which melted at  $252^{\circ}-256^{\circ}$ . One crystallization from water raised the melting point to a constant value of  $259.4^{\circ}-260.2^{\circ}$ C.

Anal. Calc. for  $C_{21}H_{20}N_{12}O_{15}$ : C, 37.06; H, 2.97; N, 24.69. Found: C, 36.88; H. 3.02; N, 24.55.

### Phenol-2,4-diguanidine

A mixture of 6.4 gm. (0.152 mole) of cyanamide and 13.05 gm. (0.066 mole) of 2,4-diaminophenol dihydrochloride in 32 cc. of absolute ethanol was refluxed under nitrogen for four hours. The alcohol was removed *in vacuo* to give a purple colored, semisolid residue. This residue was treated with aqueous sul-

\*\*\* Microanalyses by C. W. Beazley, Skokie, Ill.

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phuric acid solution which contained 6.11 cc. of sulphuric acid (sp. gr. 1.84) in 110 cc. of water. An immediate precipitate of phenol-2,4-diguanidinium sulphate was obtained in 69.8% (14.12 gm.) yield. The crude product appeared to decompose at  $282^{\circ}-286^{\circ}$ C. When this material was crystallized from 5% sulphuric acid solution, crystals were obtained which charred at  $287^{\circ}-289^{\circ}$ C. The decomposition point was indefinite.

Anal Calc. for C<sub>8</sub>H<sub>14</sub>N<sub>6</sub>O<sub>5</sub>S: C, 31.40; H, 4.58; N, 27.46. Found: C, 31.16; H, 4.89; N, 27.65.

A 1 gm. sample of the sulphate was dissolved in water and converted to the picrate in the usual manner. The melting point of 210°-220°C. of the crude picrate was raised to a constant value of 219.5°-220°C. by two crystallizations from water, yield 0.47 gm.

Anal. Calc. for C<sub>20</sub>H<sub>18</sub>N<sub>12</sub>O<sub>15</sub>: C, 36.00; H, 2.73; N, 25.20. Found: C, 35.83; H, 2.91; N. 25.01.

1. SAFIR, S. R., KUSHNER, S., BRANCONE, L. M., and SUBBAROW, Y. J. Org. Chem. 13: 924. 1948.

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A. F. McKay W. G. Hatton