

TABLE I  
 PROPERTIES OF NEW SUBSTANCES

No.	Solvent	M. p., °C.	Yield, %	Empirical formula	Analyses, %	
					Calcd.	Found
XI	Acetic acid	265-266	80	C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> O <sub>8</sub> S		
XII	Alcohol	205-206	70	C <sub>12</sub> H <sub>11</sub> N <sub>4</sub> O <sub>8</sub> S	N, 13.6	N, 13.6
XIII	Benzene	120-121 <sup>a</sup>	77	C <sub>12</sub> H <sub>9</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>8</sub> S	Cl, 20.5	Cl, 20.4
XIV		188-190	79	C <sub>14</sub> H <sub>12</sub> ClN <sub>4</sub> O <sub>8</sub> S		
XV	Benzene	143-145	37	C <sub>12</sub> H <sub>9</sub> ClN <sub>4</sub> O <sub>8</sub> S	N, 8.5	N, 8.4
XVI	Benzene	155-156	47	C <sub>14</sub> H <sub>11</sub> ClN <sub>4</sub> O <sub>8</sub> S	N, 8.2	N, 8.0
XVII	Water	174-175	80	C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>8</sub> S	N, 22.5	N, 22.6
XVIII	Water	125	84	C <sub>8</sub> H <sub>9</sub> ClN <sub>4</sub> O <sub>8</sub> S	N, 10.0	N, 10.2
XIX	Water	158	85	C <sub>10</sub> H <sub>13</sub> N <sub>4</sub> O <sub>8</sub> S	N, 13.8	N, 13.6
XX	Alcohol	213-214	28	C <sub>7</sub> H <sub>7</sub> N <sub>4</sub> O <sub>8</sub> S	N, 21.3	N, 20.8
XXI	Alcohol	221	44	C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>8</sub> S	N, 19.9	N, 19.5
XXII	Water	236-237	71	C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>8</sub> S	N, 28.3	N, 28.3
XXIII		222 <sup>b</sup>	50	C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>8</sub> S	N, 26.2	N, 26.2
XXIV		228 <sup>b</sup>	70	C <sub>12</sub> H <sub>16</sub> N <sub>4</sub> O <sub>8</sub> S	N, 18.3	N, 18.1
XXV		168 <sup>b</sup>	20	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O <sub>8</sub> S	N, 21.7	N, 21.9
XXVI		265 <sup>b</sup>	54	C <sub>12</sub> H <sub>11</sub> N <sub>4</sub> O <sub>8</sub> S <sub>2</sub>	N, 13.1	N, 12.8
XXVII			68	C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> O <sub>8</sub> S <sub>2</sub>		
XXVIII		240-242 <sup>b</sup>	95	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub> O <sub>8</sub> S <sub>2</sub>	{ C, 49.2 H, 3.5 S, 26.9	{ C, 48.8 H, 3.6 S, 25.1
XXIX		208-210 <sup>b</sup>	55	C <sub>12</sub> H <sub>9</sub> ClN <sub>4</sub> O <sub>8</sub> S <sub>2</sub>	S, 28.5	S, 27.8
XXX		284-285 <sup>b</sup>	38	C <sub>15</sub> H <sub>13</sub> N <sub>4</sub> O <sub>8</sub> S <sub>2</sub> <sup>c</sup>	N, 8.2	N, 8.3
XXXI	Alcohol	246-248 <sup>b</sup>	53	C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O <sub>8</sub> S <sub>2</sub>		
XXXII		218-220 <sup>b</sup>	65	C <sub>14</sub> H <sub>12</sub> N <sub>4</sub> O <sub>8</sub> S <sub>2</sub>		

<sup>a</sup> Prepared in acetone, using two equivalents of the amine instead of acetic acid and sodium acetate. <sup>b</sup> With decomposition. <sup>c</sup> Upon hydrolysis the free amine, m. p. 230-232°, <sup>b</sup> was formed.

three hours. After filtering, the filtrate (at 20°) was acidified. The remainder of the treatment was similar to that in the previous example.

By a similar procedure there were prepared 2-mercapto-5-sulfon-(4'-acetaminoanilido)-benzothiazole (XXX; X, R = 4-acetaminophenyl), 2-mercapto-5-sulfon-(2'-hydroxyanilido)-benzothiazole (XXXI; X, R = 2-hydroxyphenyl), and 2-mercapto-5-sulfon-(2'-hydroxy-4'-methyl-anilido)-benzothiazole (XXXII; X, R = 2-hydroxy-4-methylphenyl).

### Summary

A series of reactions is described, by which

it is possible to obtain in considerable variety the hitherto unknown sulfonamides in the benzimidazole, benzotriazole, and benzothiazole series.

By these procedures there have been prepared 5-sulfonamidobenzimidazoles, 5-sulfonamidobenzotriazole, 6-sulfonamidobenzazimidoles, 2-mercapto-5-sulfonamidobenzimidazoles and 2-mercapto-5-sulfonamidobenzothiazoles.

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## NOTES

### 1,3:2,4-Dibenzylidene-D-sorbitol

By S. J. ANGYAL AND J. V. LAWLER

In their recent exhaustive paper, Wolfe, Hann and Hudson<sup>1</sup> proved that in dibenzylidene-D-sorbitol (m. p. 219-220°) the benzylidene groups are attached to carbon atoms 1,2,3,4 of D-sorbitol. They were unable, however, to assign a definite structure.

At the time their paper reached us, we were engaged in similar research. Our results agree with theirs, but in one respect we were able to go

(1) Wolfe, Hann and Hudson. *THIS JOURNAL*, **64**, 1493 (1942).

further. By careful hydrolysis of dibenzylidene-D-sorbitol with acetic acid in alcohol, we were able to isolate a monobenzylidene-D-sorbitol identical with Vargha's 2,4-monobenzylidene-D-sorbitol.<sup>2</sup> As under these mild conditions no migration is likely, we feel entitled to assign the 1,3:2,4 structure to dibenzylidene-D-sorbitol.

In a similar way we obtained 1,3:2,4-dibenzylidene-D-sorbitol from tribenzylidene-D-sorbitol,<sup>3</sup> which proves that the latter has the structure 1,3:2,4:5,6-tribenzylidene-D-sorbitol.

(2) Vargha, *Ber.*, **66**, 23, 1337 (1935).

(3) Karrer and Büchi, *Helv. Chim. Acta*, **20**, 86 (1937).

Neither during the synthesis from sorbitol and benzaldehyde, nor during hydrolysis experiments, did we encounter another isomer of dibenzylidene-D-sorbitol, such as the one described by Meunier,<sup>4</sup> m. p. 162°. This substance was probably a mixture of di- and tri-benzylidene-D-sorbitols.

In the experimental part we give improved physical constants of mono- and tri-benzylidene-D-sorbitol and of 5,6-diacetyl-1,3:2,4-dibenzylidene-D-sorbitol.

### Experimental<sup>5</sup>

**2,4-Monobenzylidene-D-sorbitol.**—Vargha<sup>2</sup> gives m. p. 172–73°,  $[\alpha]_D^{20}$  5.3°. His sample was obviously contaminated with dibenzylidene-D-sorbitol, because he recrystallized from alcohol, in which the latter substance is fairly soluble. We prepared the mono-compound according to his directions, but recrystallized it from 6 parts of water which left the diacetal undissolved. The substance so prepared had m. p. 176–77°,  $[\alpha]_D^{17}$  –1.1° (c, 1.0) in water.

*Anal.*<sup>6</sup> Calcd. for  $C_{13}H_{18}O_6$ :  $C_6H_5CH$ , 33.33. Found:  $C_6H_5CH$ , 33.1.

**2,4-Monobenzylidene-D-sorbitol from 1,3:2,4-dibenzylidene-D-sorbitol.**—Three grams of the diacetal<sup>1</sup> was refluxed on the steam-bath with a mixture of 120 ml. 80% alcohol and 67 ml. glacial acetic acid for one hour. The solution was evaporated to dryness under reduced pressure. Thirteen ml. of water was added to the residue, the solution made carefully alkaline with sodium carbonate and boiled for a short time; 0.9 g. of unchanged dibenzylidene-D-sorbitol remained undissolved. The solution was filtered and on standing in the refrigerator deposited 0.27 g. of crystals (m. p. 173–74°, 17% yield on dibenzylidene-sorbitol not regained). After recrystallization from 1.5 ml. water the m. p. was 174–75°; mixed m. p. with the previous substance, 174–75°.

**1,3:2,4:5,6-Tribenzylidene-D-sorbitol.**—Prepared as directed by Karrer and Büchi.<sup>3</sup> Their method of purification is applicable to very small quantities only. We dissolved the crude triacetal (10 g.) in 100 ml. of chloroform, filtered from undissolved dibenzylidene-D-sorbitol and precipitated with 300 ml. alcohol (7–8 g.). The melting point of this substance shows a peculiar behavior. Pure samples recrystallized from chloroform-alcohol (1:3) or pyridine-water (3:1) have m. p.'s between 195 and 199°. Occasional pure samples had m. p.'s as low as 190°. When dissolved in pyridine and evaporated to dryness at 80° all these samples melted at 203°. Apparently the substance is dimorphous, one form melting at 203°, but we were unable to isolate the other in pure form. All pure samples have  $[\alpha]_D^{16}$  +26.9° (c, 2.0) in chloroform. Karrer and Büchi<sup>3</sup> give m. p. 191°, Simada and Matukawa<sup>7</sup> m. p. 201–204°, no rotation.

*Anal.* Calcd. for  $C_{27}H_{36}O_6$ :  $C_6H_5CH$ , 60.54. Found:  $C_6H_5CH$ , 60.4.

**1,3:2,4-Dibenzylidene-D-sorbitol from Tribenzylidene-D-sorbitol.**—Four grams of tribenzylidene-D-sorbitol (m. p. 203°) was dissolved in 40 ml. of hot chloroform, a mixture of 300 ml. 90% alcohol and 60 ml. of glacial acetic acid added, and refluxed on the steam-bath for two hours. The solution was evaporated to dryness under reduced pressure, the residue powdered and extracted, first with 50 ml. of

chloroform, then with 30 ml. of boiling water. The residue weighs 2.1 g. (76% yield), and has m. p. 220–21°. On acetylation with pyridine (10 ml.) and acetic anhydride (6 ml.) it gives a substance similar in all properties to 5,6-diacetyl-1,3:2,4-dibenzylidene-D-sorbitol.

**5,6-Diacetyl-1,3:2,4-dibenzylidene-D-sorbitol.**—This substance shows the same peculiar behavior of its melting point as tribenzylidene-D-sorbitol. Samples from benzene or acetone have m. p.'s between 202 and 206°. On evaporation from pyridine at 80° it melts at 208–209°. Wolfe, Hann and Hudson<sup>1</sup> report 201–204°.

*Anal.* Calcd. for  $C_{24}H_{28}O_8$ :  $C_6H_5CH$ , 40.73. Found:  $C_6H_5CH$ , 40.8.

RESEARCH LABORATORIES

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### An Orange-colored Pigment of Cottonseed

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We have isolated an orange-colored pigment from cottonseed by the following procedure. An ethereal extract of cottonseed was re-extracted with a dilute aqueous solution of sodium hydroxide containing sodium dithionite ( $Na_2S_2O_4$ ). The yellow-colored ethereal layer which separated from the aqueous extract when it was exactly neutralized with concentrated hydrochloric acid was withdrawn. Addition of an equal volume of glacial acetic acid to the ethereal solution caused the precipitation of gossypol "acetate" within a few minutes. When the filtrate was allowed to stand for about a week, an orange-colored solid slowly precipitated. This solid was extracted with hot acetone from which orange-colored crystals precipitated on cooling. The product was recrystallized first from hot acetone and finally from a mixture of hot chloroform and ether.

The orange-colored pigment differs markedly from gossypol. It is less soluble than gossypol in most organic solvents. It melts at 212° (cor.) to form a more deeply colored solid, which melts with decomposition at 238–239° (cor.). It is insoluble in alkali. It does not form a precipitate with aniline, reduce Fehling solution, or give a positive fuchsin-aldehyde test. The orange-colored pigment reacts with hydroxylamine and with dinitrophenylhydrazine, but the products differ in melting point from the corresponding products obtained with gossypol.

The orange-colored pigment forms a brilliant yellow solution in concentrated sulfuric acid which slowly changes to the scarlet color characteristic of gossypol in sulfuric acid.

The absorption spectrum of a chloroform solution of the orange-colored pigment exhibits a well defined maximum at 435  $m\mu$ , whereas that of gossypol occurs at 365  $m\mu$ .<sup>1</sup> The unstable reaction product of the orange-colored pigment with antimony trichloride has an absorption maximum at 450–460  $m\mu$ ; whereas that of gossypol exhibits two maxima, one at 380  $m\mu$  and the other at 510–

(4) Meunier, *Ann. chim. phys.*, [6] **22**, 412 (1891).

(5) All melting points are corrected.

(6) For the benzylidene determination ca. 100 mg. of the substance was dissolved in 5 ml. of hot glacial acetic acid in an atmosphere of nitrogen. Forty ml. of a 0.5% solution of 2,4-dinitrophenylhydrazine in *N* sulfuric acid was added, and the solution heated on a steam-bath under reflux for one hour. After cooling in ice the precipitate was collected in a Gooch crucible and dried *in vacuo* at 70°: wt. of precipitate  $\times 0.3147$  = benzylidene.

(7) Simada and Matukawa, *C. A.*, **33**, 533<sup>s</sup> (1939).

(1) Boatner, *Oil & Soap*, **21**, 10–15 (1944).