

dyes from the trisulfide bases from mustard gas show some tendency towards being direct, as the colors do not wash out in cold water. The mono-sulfides are poorer, and in the case of the sulfones practically all of the color washes out in cold water. On the other hand, all of them are removed in boiling water.

Table XV gives the colors of these dyes on cotton. Here also the color effect produced by the sulfide and sulfone groups is the same as with the acid dyes described above.

TABLE XV
COLORS OF DYES FROM DIAMINE BASES COUPLED WITH SEVERAL INTERMEDIATES AND DYED OVER COTTON

Intermediates	Benzidine	—S—	—SO ₂ —	=(SCH ₂ CH ₂) ₂ S
Naphthionic acid	Red	Burnt orange	Burnt orange	Gold
Gamma-acid	Violet	Claret	Claret	Maroon
H-acid	Blue	Blue	Lilac	Violet

Summary

A series of bases, p -NH₂C₆H₄SR, has been made and these have been diazotized and coupled with R-salt to find the effect of changes in the radical R on the color. Dyes have been made from p -toluidine, p -anisidine, p -thioanisidine and its sulfone by diazotizing and coupling with a number of intermediates. It has been found that —SCH₃ > —OCH₃ > —CH₃ > —SO₂CH₃ act as auxochromes.

Diamine bases of the type p,p' -NH₂C₆H₄-X-C₆H₄NH₂ have been made in which X is —S—, —SO₂—, —SCH₂—, —SCH₂S—, —SCH₂CH₂S—, —SCH₂CH₂SCH₂CH₂S—, etc., and these were tetrazotized and coupled with various intermediates to find the effect of the group between the two rings on the color of the dyes. These bases do not resemble benzidine in giving fast cotton dyes.

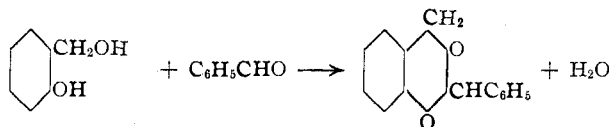
BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]
ARYL 1,3-BENZO-DIOXANES (ARYL METHYLENE-SALIGENINS)

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In a contribution from this Laboratory on the structure of disalicyl aldehyde,¹ it was shown that saligenin condensed readily with benzaldehyde to yield 2-phenyl-1,3-benzo-dioxane according to the following equation.



¹ Adams, Fogler and Kreger, THIS JOURNAL, 44, 1126 (1922).

Since a condensation of this type has not been previously described a study has been made of the condensation of certain substituted benzaldehydes with saligenin and substituted saligenins. It has been found that the reaction is quite general and takes place with the greatest ease. Whereas it was necessary to have present a catalyst, such as a small amount of benzoic acid, when benzaldehyde condensed with saligenin, no catalyst was found necessary with the substituted compounds. Cinnamic aldehyde condensed like the aromatic aldehydes and it is probable that any α,β -unsaturated aldehyde will react similarly. Simple aliphatic aldehydes did not condense with saligenin to give dioxanes under similar conditions.

The condensation to form dioxanes is a type of acetal formation and resembles the condensation of benzaldehyde with trimethylene glycol² or trimethylene glycol derivatives. The only difference is that in saligenin one of the hydroxyl groups is a phenol and the other is an alcohol. Since it has been shown that aromatic aldehydes form acetals with phenols under proper conditions, and these are intermediates in the formation of triphenyl methane compounds, it is not surprising that aromatic aldehydes condense with saligenin to form dioxanes. Apparently there is no tendency for the products formed to rearrange into triphenyl methane or analogous compounds.

The 2-aryl-1,3-benzo-dioxanes are formed in very good yields (60–95%). They are white crystalline compounds and, like simple acetals, very stable toward alkalis but unstable toward acids, with the formation of saligenin and aldehyde.

Experimental Part

General Method for the Preparation of 1,3-Benzo-dioxanes.—A mixture of 1 molecular equivalent of saligenin or substituted saligenin and benzaldehyde or substituted benzaldehyde was heated on a steam-bath until a homogeneous liquid resulted. This required generally 5 to 30 minutes but in the case of nitrobenzaldehyde and saligenin, almost 2 hours. After the heating, the reaction mixtures were allowed to stand at room temperature until they solidified, the time required varying from a few minutes to 8 to 10 hours. The resulting solids were washed with water and crystallized from alcohol. In the cases of benzaldehyde and saligenin and nitrobenzaldehyde and saligenin, benzoic acid was used as a catalyst. In these latter experiments, consequently, the reaction mixtures were washed with sodium carbonate and then with water before crystallization was attempted.

The condensation of nitrosaligenin with benzaldehyde and substituted benzaldehyde was attempted. No definite condensation products could be isolated and in one case apparently no reaction took place.

² Fischer, *Ber.*, 27, 1537 (1896).

		1,3-BENZO-DIOXANES	
Condensed products		M. p. °C.	Analyses
1. Saligenin <i>p</i> -Chlorobenzaldehyde		107-107.5	Subs., 0.1303: CO ₂ , 0.3247; H ₂ O, 0.0058. Calc. for C ₁₄ H ₁₁ O ₂ Cl: C, 68.15; H, 4.46. Found: C, 67.96; H, 4.43.
2. Saligenin <i>p</i> -Bromobenzaldehyde		117-117.5	Subs., 0.1183: CO ₂ , 0.2507; H ₂ O, 0.0043. Calc. for C ₁₄ H ₁₁ O ₂ Br: C, 57.73; H, 3.78. Found: C, 57.79; H, 3.68.
3. Saligenin <i>m</i> -Nitrobenzaldehyde		88-89.5	Subs., 0.1815: N ₂ (corr.), 15.45 cc. Calc. for C ₁₄ H ₁₁ O ₄ N: N, 5.45. Found: 5.32.
4. Bromosaligenin 5-(Br)-2-(HO)C ₆ H ₄ CH ₂ OH Benzaldehyde		85	Subs., 0.5000: CO ₂ , 650.1 cc. (31.5°, 741 mm.). Calc. for C ₁₄ H ₁₁ O ₂ Br: C, 57.73. Found: 58.00.
5. Bromosaligenin <i>p</i> -Chlorobenzaldehyde		147-148	Subs., 0.5000: CO ₂ , 584.4 cc. (32.5°, 741 mm.). Calc. for C ₁₄ H ₁₀ O ₂ Br-Cl: C, 51.62. Found: 51.82.
6. Bromosaligenin <i>p</i> -Bromobenzaldehyde		143-144	Subs., 0.5000: CO ₂ , 506.8 cc. (31.5°, 739 mm.). Calc. for C ₁₄ H ₁₀ O ₂ Br ₂ : C, 45.42. Found: 45.04.
7. Bromosaligenin Cinnamic aldehyde		118-120	Subs., 0.4000: CO ₂ , 537.2 cc. (29.3°, 741 mm.). Calc. for C ₁₆ H ₁₃ O ₂ Br: C, 60.57. Found: 60.75.
8. Methyl saligenin 5-(CH ₃)-2-(HO)C ₆ H ₄ CH ₂ OH Benzaldehyde		90	Subs., 0.2000: CO ₂ , 338.0 cc. (22.5°, 743 mm.). Calc. for C ₁₅ H ₁₄ O ₂ : C, 79.64. Found: 79.59.
9. Methyl saligenin <i>p</i> -Bromobenzaldehyde		130	Subs., 0.2000: AgBr, 0.1221. Calc. for C ₁₅ H ₁₃ O ₂ Br: Br, 26.22. Found: 25.97.

Cinnamic aldehyde and saligenin did not give a solid product.

Formaldehyde, acetaldehyde and butyraldehyde were condensed in succession with saligenin but in no case was a dioxan obtained.

Saligenin.—Saligenin was prepared by the reduction of salicyl aldehyde according to the method of Voorhees and Adams.³

Bromosaligenin,⁴ 5-Br-2-HOC₆H₄CH₂OH.—Bromosaligenin was prepared by a slight modification of the method of Auwers.

A solution was made of 50 g. (1 molecular equivalent) of saligenin in 2.5 liters of water in a 12-liter flask. This solution was cooled to 5-10° and kept cold and stirred mechanically during the addition of 9 liters of bromine water containing 65 g. (1 molecular equivalent) of bromine, requiring about 2 hours. The solution was filtered to remove a small amount of tar and was then extracted with 3 to 4 liters of ether. After the ether had been dried it was distilled and a yellow liquid remained which solidified as it cooled. After crystallization from benzene there was obtained 44 g. of white plates which after a

³ Voorhees and Adams, *THIS JOURNAL*, **44**, 1397 (1922). See also Carothers and Adams, *ibid.*, **45**, 1071 (1923).

⁴ Auwers and Büttner, *Ann.*, **302**, 131, 138 (1898).

second crystallization melted at 107–109°. This was used in the condensation mentioned above.

p-Homosaligenin, 5-CH₃-2-HOC₆H₄CH₂OH.—Homosaligenin is difficult to prepare by any of the methods now described in the literature. The best two are treating *p*-cresol with formaldehyde, and the reduction of homosalicylaldehyde with sodium amalgam. A most satisfactory method was reduction of homosalicylaldehyde with hydrogen and platinum oxide according to the general method described by Carothers and Adams.⁵

A solution of 27.2 g. of *p*-homosalicylaldehyde in 100 cc. of alcohol was treated with 0.23 g. of platinum oxide and 0.1 cc. of *N* ferrous chloride solution. The mixture was reduced in the usual way, the time required being about 40 minutes when the hydrogen was passed in under a pressure of about 1.5 atmospheres. The yield was quantitative. The platinum was filtered off, the solution was evaporated and the product recrystallized. It then melted at 105°.

Summary

1. It has been found that benzaldehyde and substituted benzaldehydes condense with saligenin and substituted saligenins to yield 2-aryl-1,3-benzo-dioxanes.

2. The condensations take place with the greatest ease and generally without the addition of a catalyst. In the case of benzaldehyde and saligenin, and of nitrobenzaldehyde and saligenin the presence of benzoic acid greatly speeded up the reaction and gave the best results.

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PROPERTIES OF DYED MATERIALS

BY H. WALES

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Absorption Spectrum and Its Relationship to Color

Ever since the discovery of artificial colors, attempts have been made to find some relationship between the color and the chemical constitution. For some classes of dyes theories have been worked out with fair success. In practically every case, however, the "color" has been determined by means of the position of the absorption band or bands as determined with a spectroscope.¹

The author has been led to believe by some recent observations that this method is incorrect and that the location of the absorption maximum

⁵ Carothers and Adams, THIS JOURNAL, 45, 1071 (1923).

¹ Ley, "Beziehungen zwischen Farbe und Konstitution," F. Hirzel, Leipzig, 1911. Watson, "Color in Relation to Chemical Constitution," Longmans, Green and Co., 1918.