

Studies in Azotriphenylcarbinol Dyes.

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Considerable interest is attached to the investigation of the joint effect of different chromophores specially the azo- and triphenyl carbinol groups contained in the molecule of a dyestuff. This type of triphenylcarbinol dyes, containing one triphenylcarbinol group in the *para*-position to an azo-group and without any auxochromic group in the molecule, has been previously studied by Green and Sen (*J. Chem. Soc.*, 1912, 101, 1113).

The effect of multiplying the number of chromophores, specially the azo-group, in this type of dyestuff has been ascertained later by Sen and Sett (*J. Amer. Chem. Soc.*, 1924, 46, 111). Now further studies in azotriphenylcarbinol dyes have been made with a view (1) to ascertain the effect of the introduction of an additional triphenylcarbinol group on the colour and dyeing properties, and (2) to determine the influence of an additional auxochrome (OH) in the *para*-position to the azo-group.

The azotriphenylmethane dyestuffs, containing two triphenylcarbinol groups in the *para*-positions to the azo-group have been prepared by the condensation of the dialdehyde (azobenzaldehyde sulphonic acid, *J. Indian Chem. Soc.*, 1930, 7, 14) with the hydroxyacids such as, salicylic acid, 2-hydroxy-*m*-toluic acid and 2-hydroxy-*p*-toluic acid by means of concentrated sulphuric acid (*d* 1.84, free from nitric acid) in the cold. The reaction takes place between one molecule of the dialdehyde and four molecules of the hydroxyacid. The leuco-compounds are oxidized to azotriphenylcarbinol compounds by means of sulphuric acid solution of nitrosyl sulphate. To complete the reaction it is necessary to warm the mixture to 50° for about 3 hours.

The leuco-compounds are yellow dyestuffs and produce on wool yellow shades considerably lighter than the shade (orange) obtained with the dialdehyde itself. This shows that too much complexity of the molecules seems to have an effect similar to that of too much multiplication of chromophores. It is a curious fact that only the leuco-compound of 2-hydroxy-*m*-toluic acid produces on

* The delay in the publication of the paper is due to the sudden death of one of the authors.

wool a pink shade even when it is prepared with exclusion of air in an atmosphere of carbon dioxide.

Wool is dyed directly in red shades by the carbinol dyes excepting that obtained from the leuco-condensation product of the dialdehyde with 2-hydroxy-*p*-toluic acid, which has very feeble dyeing properties and produces a light chocolate shade, showing the marked effect of the position of the CH₃-group on the colour and dyeing property. With different mordants on wool, different shades are produced: tin, bright red; copper, bluish-red; aluminium, reddish-violet; iron, reddish-black. It is very interesting to note that the yellow shade on wool, produced by the leuco-compounds, is changed to black on after-chroming, passing through violet to green (Green and Sen, *loc. cit.*).

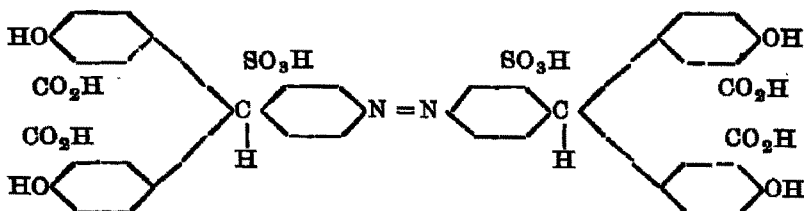
Next to study the influence of an additional auxochrome (OH) in the *para*-position to the azo-group, salicyl-azobenzaldehyde-sulphonic acid (*J. Indian Chem. Soc.*, 1930, 7, 16) has been condensed with the hydroxy-acids in the manner described in the experimental part.

The shades (yellow), produced by the leuco-compounds are also lighter than the shade (orange) obtained with the mono-azo-aldehyde; and it is presumably due to the same cause (*i.e.*, too much complexity of the molecule). It may be pointed out here that the leuco-condensation product of 2-hydroxy-*p*-toluic acid does not produce the shade (pink) like that of its condensation product with the dialdehyde. The dyeing property of the oxidized condensation product of 2-hydroxy-*m*-toluic acid with the monoaldehyde almost resembles that of the corresponding compound of phenetole-azo-benzaldehyde-sulphonic acid obtained by Green and Sen (*loc. cit.*) but the shade of the corresponding compound (containing two triphenylcarbinol groups) from the dialdehyde is slightly deeper (blue), whereas the introduction of an additional azo-group makes the colour lighter (Sen and Sett, *loc. cit.*) The same peculiarity, *i.e.*, feeble dyeing property has also been observed in the oxidised condensation product of mono-azo-aldehyde and 2-hydroxy-*p*-toluic acid, which produces on wool a light chocolate shade. This fully confirms the observation that the change in the position of CH₃-group in the molecule has a very marked effect on the dyeing property.

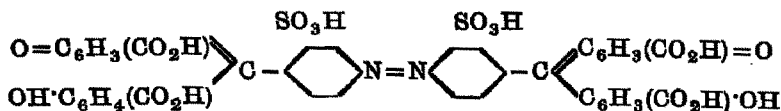
EXPERIMENTAL.

Dyes from Azobenzaldehyde-sulphonic Acid.

Condensation product with salicylic acid (Azodihydroxydicarboxytriphenylmethane-sulphonic acid) :



A mixture of the azo-aldehyde (3.3 g.) and salicylic acid (4.2 g.) was stirred with concentrated sulphuric acid ($d\ 1.84$, 15 c.c.) for 20 to 30 minutes, when it became pasty and very hot. The mixture is allowed to remain overnight at the room temperature and poured into powdered ice, the precipitate is filtered and washed with a little cold water acidulated with hydrochloric acid. It is finally dissolved in hot water (170 c.c.) and reprecipitated with concentrated hydrochloric acid; yellow microscopic powder, very soluble in cold water and can easily be precipitated by hydrochloric acid; dyes wool a yellow shade from an acid bath and on after-chroming the colour of the 3% dyed wool changes to violet-black. (Found: N, 3.22; S, 7.10. $C_{42}H_{30}O_{18}N_2S_2$ requires N, 3.06; S, 7.00 per cent.)

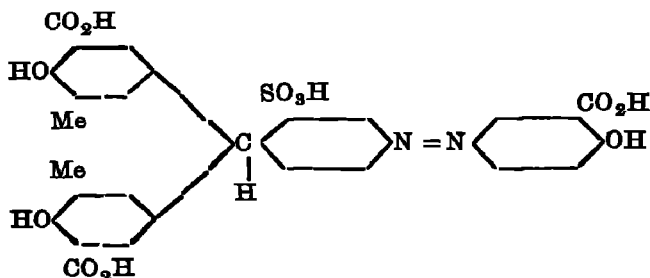
Oxidation product of the above compound.—

The azo-aldehyde (3.3 g.) is condensed with salicylic acid (4.2 g.) by means of sulphuric acid (15 c.c.). To the sulphuric acid solution of the leuco-compound a solution of nitrosyl sulphate is directly added and the oxidation completed by slowly warming the mixture to 50° for about three hours. The solution is then poured into iced water (110 c.c.), the precipitate is filtered off and washed with acidified water. It is finally dissolved in hot water (160 c. c.) and reprecipitated by hydrochloric acid; red micro-crystalline powder,

soluble in cold water (red solution); dyes wool a red shade. (Found: N, 2.98; S, 7.30. $C_{43}H_{26}O_{18}N_2S_2$ requires N, 3.08; S, 7.03 per cent.)

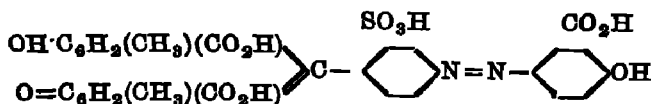
Dyes from Salicylazobenzaldehyde-sulphonic Acid.

Condensation product with cresotinic acid (COOH: OH: CH₃: 1: 2 r. 3) (Salicylazodihydroxydimethyldicarboxytriphenylmethane sulphonic acid).



The condensation is effected in the manner described before; reddish-orange powder, soluble in cold water (yellow solution); dyes wool a yellow shade and on after-chroming a striking series of changes take place and the colour changes finally to black. (Found: N, 4.82. $C_{30}H_{24}O_{12}N_2S$ requires N, 4.42 per cent.)

Oxidation product.—



The oxidation is effected with nitrosyl sulphate; red powder, readily soluble in cold water giving a red solution; dyes wool a red shade. (Found: N, 4.27. $C_{30}H_{22}O_{12}N_2S$ requires N, 4.40 per cent.)

Other azotriphenylmethane dyes from azobenzaldehyde-sulphonic acid and from salicylazobenzaldehyde-sulphonic acid are listed in the following table.

Summary.

(1) In the case of leuco-azotriphenylmethane dyes, the shades (yellow) on wool are lighter than the shades (orange) produced on wool by the aldehydes; this may be attributed to too much complexity of the molecule.

(2) In the case of azotriphenylcarbinol dyes, the depth of shade produced on wool seems to be slightly increased by an addition of a triphenylcarbinol group.

(3) The CH_3 -group in the *meta*-position to the OH-group has a remarkable effect in decreasing the intensity of colour and also the dyeing properties of azotriphenylcarbinol dyes.

(4) The influence of an additional OH-group in the *para*-position to the azo-group is practically nil.

TABLE I.

Formulae.	Preparation.	Analysis.		Properties.
		Found %	Calc. %	
$C_{10}H_{11}O_4N_2S_2$ (leuco-base)	The asoaldehyde-sulphonic acid + cresotinic acid (COOH : OH : CH_3 : 1 : 2 : 3) + conc. H_2SO_4 .	N, 2'80 S, 6'71	N, 2'89 S, 6'60	Reddish-orange powder, easily soluble in water, can be precipitated with HCl.
Oxidation product— $C_{10}H_9O_4N_2S_2$	By oxidation with nitrosyl sulphate.	N, 2'81 S, 6'81	N, 2'90 S, 6'68	Dark red powder.
$C_{10}H_9O_4N_2S_2$ (leuco-base)	The asoaldehyde-sulphonic acid + cresotinic acid (COOH : OH : OH_2 : 1 : 2 : 4) + conc. H_2SO_4 .	N, 2'80 S, 6'82	N, 2'89 S, 6'60	Yellow powder, sparingly soluble in cold water.
Oxidation product— $C_{10}H_7O_4N_2S_2$	By oxidation with nitrosyl sulphate.	N, 2'98 S, 6'90	N, 2'80 S, 6'68	Reddish-brown powder, readily soluble in water.
$C_{10}H_7O_4N_2S_2$ (leuco-base)	Salicylazobenzaldehyde-sulphonic acid + cresotinic acid (COOH : OH : OH_2 : 1 : 2 : 4) + conc. H_2SO_4 .	N, 4'36	N, 4'42	Yellow, black on after-chroming.
Oxidation product— $C_{10}H_5O_4N_2S_2$	By oxidation with nitrosyl sulphate.	N, 4'47	N, 4'40	Light chocolate.

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Received May 12, 1927.