

517. *Steric Effects in Di- and Tri-arylmethanes. Part VI.\**  
*Nucleophilic Replacements in Triphenylmethane Dyes.*

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Steric hindrance of the central carbon atom in basic triphenylmethane dyes facilitates replacement of a terminal dimethylamino-group by a hydroxy-group with formation of a fuchsone. Sufficient hindrance also permits replacement of a dimethylamino-group in the dye base.

THE possibility of achieving nucleophilic replacements in triarylcarbonium ions is demonstrated by the formation of *pp'*-dibromo-*p''*-chlorotriphenylmethyl bromide from *pp'p''*-tribromotriphenylmethyl chloride in liquid sulphur dioxide,<sup>1</sup> but examples are rare. Nucleophilic replacements are, however, quite common in basic triphenylmethane dyes, one of the earliest examples being the formation<sup>2</sup> of Diphenylamine Blue base (I; R = Ph) by heating Pararosanine base (I; R = H) with aniline in the presence of a little benzoic acid which presumably acts by forming the reactive Pararosanine ion. Other *para*-groups that readily undergo replacement are the ethoxy-, chloro-, and sulphonyl-group,<sup>2</sup> and it is now shown that the *p*-dimethylamino-group can be replaced by the hydroxy-group.

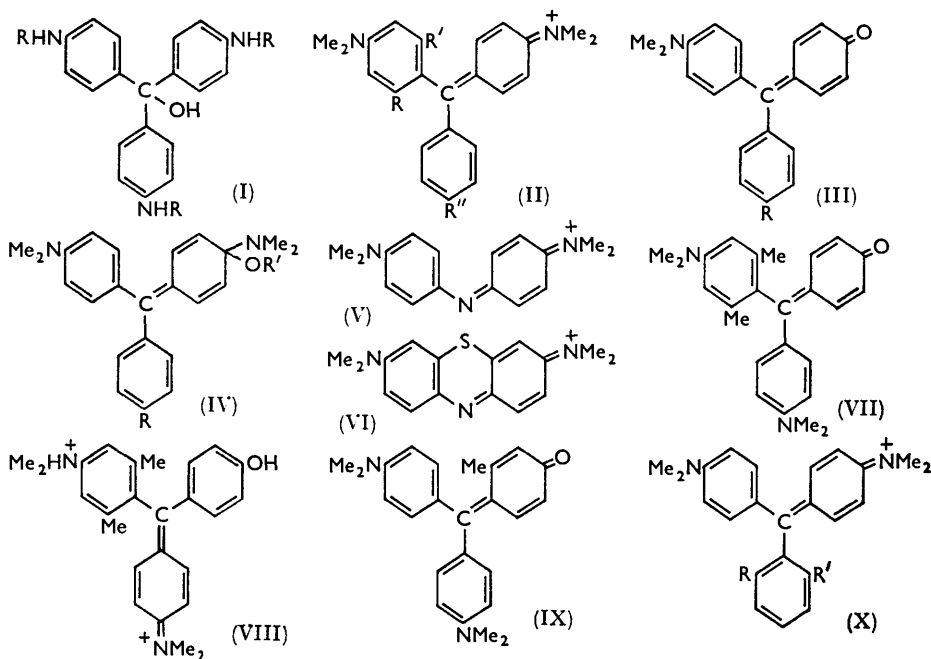
Addition of dilute, aqueous sodium hydroxide to Crystal Violet (II; R = R' = H,

\* Part V, *J.*, 1961, 1529.

<sup>1</sup> Gomberg, *Ber.*, 1909, **42**, 406.

<sup>2</sup> Thorpe, "Dictionary of Applied Chemistry," Longmans, Green and Co., London, 1954, Vol. II, p. 689.

$R'' = NMe_2$ ), Malachite Green (II; all R's = H), or such of their derivatives as are not highly hindered at the central carbon atom, yields the dye base contaminated by reddish-brown impurities which are probably fuchsons derivatives of type (III;  $R = NMe_2$  or H). These dye bases are stable to alkali and the fuchsons are assumed to arise through a competing reaction between the dye ion and the hydroxide ion, leading to an intermediate (IV;  $R = NMe_2$  or H,  $R' = H$ ) which subsequently eliminates dimethylamine. This formulation of the reaction is consistent with the complete absence of red impurities



in the methyl ethers of the dye bases prepared by treating these dyes with methanolic sodium methoxide; the intermediate (IV;  $R = NMe_2$  or H,  $R' = Me$ ) would not eliminate trimethylamine and thus form the fuchson. This smooth preparation of pure methyl ethers has been utilised to obtain spectroscopically pure dyes.<sup>3</sup> Addition of a strong solution of sodium hydroxide to Crystal Violet gives considerable amounts of a reddish-brown material<sup>4</sup> which is probably a secondary product formed by the action of strong alkali on the 4',4''-bisdimethylaminofuchson (III;  $R = NMe_2$ ) first formed; the last compound can be obtained by the basification of the 4-hydroxy-derivative of Malachite Green<sup>5</sup> and it undergoes change readily.

Replacement of the dimethylamino-group becomes predominant whenever dye-base formation is prevented or made difficult. Thus Bindschedler's Green (V) and Methylene Blue (VI), in which the presence of a central nitrogen atom instead of a central carbon atom prevents the formation of non-ionised base, readily lose dimethylamine with alkali,<sup>6</sup> and the highly hindered 2,6-dimethyl derivative of Crystal Violet (II;  $R = R' = Me$ ,  $R'' = NMe_2$ ) gives 4',4''-bisdimethylamino-2',6'-dimethylfuchson (VII) quantitatively after several hours, whereas with methanolic sodium methoxide the dye is unchanged after 14 days. The structure of this fuchson is established by its absorption spectra in different solvents. In non-acidic solvents the single band in the visible region shows a

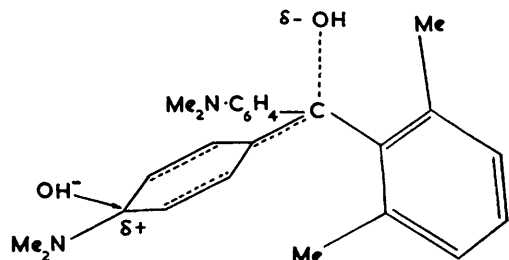
<sup>3</sup> Barker, Bride, Hallas, and Stamp, *J.*, 1961, 1285.

<sup>4</sup> Freundlich and Loser, *Z. phys. Chem.*, 1906, 59, 303.

<sup>5</sup> Ghosh and Watson, *J.*, 1917, 826.

<sup>6</sup> Möhlau, *Ber.*, 1883, 16, 2855; Bernthsen, *Ber.*, 1906, 39, 1808.

bathochromic shift when a solvent of higher dielectric constant is used [*e.g.*,  $\lambda_{\max}$  (in  $C_6H_6$ ) 477  $m\mu$ ,  $\epsilon$  31,400;  $\lambda_{\max}$  (in MeOH) 562  $m\mu$ ,  $\epsilon$  51,000], an effect which is consistent with the aminofuchsones structure. In 98% acetic acid two bands are shown in the visible region. The first of these ( $\lambda_{\max}$  635  $m\mu$ ;  $\epsilon$  28,300) is the first band of the univalent ion (II; R = R' = Me, R'' = OH), whereas the second ( $\lambda_{\max}$  500  $m\mu$ ;  $\epsilon$  33,300) is probably the second band of the same ion superimposed on the first band of the bivalent ion (VIII). The latter ion ( $\lambda_{\max}$  507  $m\mu$ ;  $\epsilon$  38,000) is formed completely when the acidity of the acetic acid is increased by addition of water or hydrochloric acid, and this ready formation of the bivalent ion, coupled with the low intensity of the first band of the univalent ion, shows that the *o*-methyl groups are not situated on the quinonoid nucleus. 4',4''-Bisdimethylamino-2-methylfuchsones (IX) in acetic acid gives a normal Malachite Green spectrum.<sup>3</sup>



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The stability of the dimethylamino-group on the xylyl nucleus in the 2,6-dimethyl derivative of Crystal Violet is consistent with the view<sup>7</sup> that it is the xylyl group rather than the phenyl group which relieves steric strain by twisting about the central bond. The terminal nitrogen atom of the xylyl group is thus partially deconjugated from the central carbon atom.

The 2,6-dimethyl-, 2-*t*-butyl-, and 2-iodo-derivative of Malachite Green (X; R = R' = Me; R = H, R' = Bu<sup>t</sup>; and R = H, R' = I, respectively) with sodium hydroxide also give the corresponding fuchsones by replacement of a dimethylamino-group, and from the first of these dyes dimethylamine was isolated as the picrate, m. p. and mixed m. p. 158—160°. These fuchsones were not obtained pure but their red solutions again showed a bathochromic shift on changing from solvent benzene to solvent methanol.

With alkali under vigorous conditions, highly hindered dye bases can lose a dimethylamino-group. Thus, the 2,6-dimethyl and 2-*t*-butyl derivative of Malachite Green base, obtained from Michler's ketone and the appropriate aryl-lithium compound,<sup>3</sup> are converted into the corresponding fuchsones when boiled with aqueous-ethanolic sodium hydroxide, whereas Malachite Green base and its 2-methyl derivative are stable under these conditions. In the more highly hindered dye bases, nucleophilic replacement of a dimethylamino-group is sterically assisted by the reduction of strain which occurs on removal of the central hydroxy-group (see Figure).

#### EXPERIMENTAL

4',4''-Bisdimethylamino-2',6'-dimethylfuchsones.—A 1% aqueous solution of the 2,6-dimethyl derivative of Crystal Violet (chloride<sup>7</sup>) containing 3 equivalents of sodium hydroxide was kept for 48 hr. The red precipitate was dried and crystallised from benzene, giving the fuchsones, m. p. 214° (Found: C, 80.5; H, 7.6; N, 7.7.  $C_{25}H_{28}N_2O$  requires C, 80.6; H, 7.5; N, 7.5%).

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<sup>7</sup> Barker, Bride, and Stamp, *J.*, 1959, 3957.