267. *Steric Effects in Di- and Tri-arylmethanes. Part IV.*[1] *Electronic Absorption Spectra of α-Alkyl Derivatives of Michler's Hydrol Blue.*

By C. C. Barker and G. Hallas.

Absorption spectra of α-alkyl derivatives of Michler's Hydrol Blue (I; R = Me, Et, Pr^{n}, Pr^{i}, Bu^{n}, Bu^{i}, and Bu^{t}) have been determined for solutions in 98% acetic acid. The spectra of dimeric derivatives formed during 1—4 days in this solvent have also been determined and are discussed in terms of molecular conformation.

It was pointed out in Part III[1] of this series that the bathochromic shift of 13·5 mμ observed on passing from Michler's Hydrol Blue (I; R = H) to Malachite Green (I; R = Ph) was caused by combined electronic and steric effects of the phenyl group. In the hope that the simpler electronic effect of an alkyl group would make analysis of the spectral shifts easier, the α-alkyl derivatives of Michler's Hydrol Blue were examined. The $-E$ activity of an α-alkyl group produces a hypsochormic shift whereas the expected steric effect is bathochromic.

Michler's Hydrol Blue gives an intense first band followed by a weak second band with two peaks (Table), but the α-t-butyl derivative gives first and second bands of low but similar intensity, and the second band shows only a single peak (Table). Further, although addition of hydrochloric acid to a solution of Michler's Hydrol Blue in 98% acetic acid leads to progressive disappearance of both these bands by formation of the bivalent ion (II), addition of hydrochloric acid to the α-t-butyl derivative leads to preferential reduction of the first band and it is assumed that this band arises from the

Absorption maxima (mμ) ($10^{-4}\varepsilon$ *in parentheses*) *of derivatives of Michler's Hydrol Blue in 98% acetic acid.*

Michler's Hydrol Blue α-subst.	Fresh solution			Solution after *n* hr.		*n*
None	607·5 (14·75);	390 (0·45);	368·5 (0·50)			
Me	606 (1·09);	397·5 (0·10);	376 (0·08)			
Et	620 (1·90);	402·5 (0·21);	381 (0·17)	637·5 (0·86);	350 (1·48)	24
Pr^{n}	620 (1·04);	402·5 (0·18);	382·5 (0·16)	638 (1·23);	347·5 (1·29)	24
Pr^{i}	610 (1·41);	402 (0·20);	382·5 (0·17)	630 (0·07);	353 (0·26)	75
Bu^{n}	617·5 (0·41);[a]	402 (0·07);	381 (0·06)	638 (0·95);	346 (1·42)	60
Bu^{i}	610 (1·27);	402·5 (0·25);	383 (0·17)	637·5 (0·46;	346 (1·05)	95
Bu^{t}	617·5 (0·064);	384 (0·077);				

[a] Increased to 0·93 during 1 hr.

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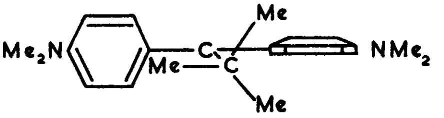
[1] Part III, *J.*, 1961, 1285.

univalent ion (I; R = Bu^t) and that the second band arises from the bivalent ion (III; R = Bu^t). There is no spectral evidence to indicate formation of the bivalent ion (III; R = H) from Michler's Hydrol Blue, and the ready formation of this type of ion from the α-t-butyl derivative can be explained by assuming that the t-butyl group causes rotation of one only of the dimethylaminophenyl groups about a central bond (see Figure).



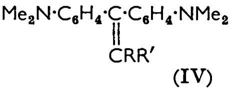
The molecular conformation of the α-t-butyl derivative of Michler's Hydrol Blue.

The resulting unsymmetrical conformation would produce two effects. First, the incompletely conjugated nitrogen atom would be protonated readily. Second, the univalent cation (I; R = Bu^t) would become electronically unsymmetrical. It is well established that by twisting the aryl nuclei about the central bonds of an electronically symmetrical cyanine a bathochromic shift is produced, whereas in an electronically unsymmetrical cyanine the shift is hypsochromic,[2] so that the effect of twisting one of the dimethylaminophenyl groups about a central bond would be to produce a bathochromic shift which with increased rotation of the aryl group would decrease and ultimately become hypsochromic. The bathochromic shift of 10 mμ brought about by the α-t-butyl group is significantly smaller than the shift of 42 mμ shown by the 2,6,2′,6′-tetramethyl derivative [3] and is consistent with the production of an unsymmetrical conformation by the t-butyl group. This argument ignores the purely electronic effect of the t-butyl and methyl groups, but these groups in the 4-position of Malachite Green produce hypsochromic shifts of only 5 and 4·5 mμ respectively.[1]

$Me_2N\cdot C_6H_4\cdot CR{:}C_6H_4{:}NMe_2^+$ (I)

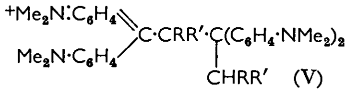
$^+Me_2HN\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot NHMe_2^+$ (II)

$^+Me_2HN\cdot C_6H_4\cdot CR{:}C_6H_4{:}NMe_2^+$ (III)



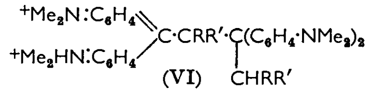
$$Me_2N\cdot C_6H_4\cdot \underset{\underset{CRR'}{\|}}{C}\cdot C_6H_4\cdot NMe_2$$

(IV)



$$\left.\begin{array}{l} ^{+}Me_2N{:}C_6H_4 \\ Me_2N\cdot C_6H_4 \end{array}\right\rangle C\cdot CRR'\cdot \underset{\underset{CHRR'}{|}}{C}(C_6H_4\cdot NMe_2)_2$$

(V)



$$\left.\begin{array}{l} ^{+}Me_2N{:}C_6H_4 \\ ^{+}Me_2HN{:}C_6H_4 \end{array}\right\rangle C\cdot CRR'\cdot \underset{\underset{CHRR'}{|}}{C}(C_6H_4\cdot NMe_2)_2$$

(VI)

(All substituents in aromatic rings are *para*.)

The low intensity of the first band of the α-t-butyl derivative also points to a lack of electronic symmetry which reduces the resonance energy of the ion (I; R = Bu^t) and thus moves the dye base–dye equilibrium in favour of the dye base. The presence of large amounts of dye base (or protonated dye base) in an ethanolic solution of the monohydrochloride of the α-t-butyl derivative is confirmed by the presence of an intense band at 262·5 mμ.

Indirect support for the unsymmetrical conformation of the α-t-butyl derivative of Michler's Hydrol Blue is provided by a study of other α-alkyl derivatives. In general, the bases of these compounds very readily form an olefin (IV) by loss of water, particularly in acid solution, so that in acetic acid the equilibrium is between olefin and the ion (I) and there is no change in hybridisation at the central carbon atom; it is the release of compressional energy upon changing the valency distribution of the central carbon atom of Michler's Hydrol from tetrahedral to trigonal that assists the formation of Michler's Hydrol Blue. Consequently, α-alkyl derivatives of Michler's Hydrol Blue give weak absorption bands in acetic acid.

A freshly prepared solution of the α-ethyl derivative of Michler's Hydrol Blue in 98% acetic acid gives absorption bands which, apart from their low intensity, are very similar

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[2] Brooker, White, Sprague, Dent, jun., and van Zandt, *Chem. Rev.*, 1947, **41**, 325.

[3] Barker, Bride, and Stamp, *J.*, 1959, 3957.

to those of the parent compound. The bathochromic shift (12·5 mμ) of the first band relative to that of Michler's Hydrol Blue reveals a steric effect apparently greater than that produced by the α-t-butyl group (10 mμ), which is consistent with the unsymmetrical conformation of the t-butyl derivative. However, the spectrum of the α-ethyl derivative in 98% acetic acid changes with time and finally (24 hr.) develops a strong band at 350 mμ (Table). Further, increasing the acidity of the solution by addition of water causes preferential reduction in the intensity of the long-wavelength band, so that two molecular species must be present in solution. This result is consistent with slow dimerisation of the olefin (IV; R = H, R′ = Me) to give a mixture of the ions (V and VI; R = H, R′ = Me). 1,1-Diphenylethylene polymerises to 1,1,3,3-tetraphenylbut-1-ene in the presence of cationic catalysts,[4] and the dimethylamino-groups in the olefin (IV) should facilitate polymerisation. The shift from 620 to 637·5 mμ shown by the first band corresponds to increased crowding in the ion (V; R = H, R′ = Me) compared with the ion (I; R = Et), and it must be assumed that, although the disposition of the dimethylaminophenyl groups is sufficiently unsymmetrical to permit formation of the protonated ion (VI; R = H, R′ = Me), the departure from symmetry is small enough for deviation from planarity to produce a marked bathochromic shift. The position of the band due to the protonated ion (VI; R = H, R′ = Me) at 350 mμ instead of at 384 mμ as in the ion (III; R = Bu^t) is consistent with a hypsochromic shift brought about by twisting the conjugated dimethylaminophenyl group about the central bond, that is, consistent with greater symmetry in the ion (VI; R = H, R′ = Me) and therefore ion (V; R = H, R′ = Me) than in ions (III and I; R = Bu^t).

Very similar behaviour is shown by the propyl, isopropyl, butyl, and isobutyl derivative of Michler's Hydrol Blue (Table). The variations in position of the first band of the monomeric ion (I) must be a function of the $-E$ activity and the steric effect of the alkyl groups, but correlation of these factors with the observed shifts is not possible. The dimeric ions (V) give first bands of essentially constant wavelength with the exception of the isopropyl derivative which gives a very weak band at somewhat shorter wavelength (Table). This dimer is also exceptionally crowded; it has a quaternary β-carbon atom and thus resembles the α-t-butyl derivative of Michler's Hydrol Blue. The bands corresponding to the protonated dimeric ion (VI) also occur at essentially the same position, but again the isopropyl derivative (VI; R = R′ = Me) gives a somewhat weaker band.

The α-methyl derivative is unique in that in acetic acid its spectrum, which closely resembles that of the parent compound, shows no change with time, implying that the dimer is not formed. This interpretation is not in accord with the fact that the β-carbon atom of this dimer carries only a single substituent so that crowding is at a minimum and dimer formation should take place most readily. When a solution of 1,1-bis-(*p*-dimethylaminophenyl)ethylene in acetic acid was kept for 48 hours and then poured into ice-cold, aqueous sodium hydroxide, the dimer was isolated, whereas addition of alkali to the dimer in acetic acid yielded only monomer, and dimer could not be isolated from a solution of monomer in acetic acid that had been kept for only 20 minutes. The dimer sublimed slowly at 200° (bath/10^{-4} mm.) without depolymerising and gave a molecular weight of 465 (micro-Rast) (theor. 532). Clearly, if preceding views about the relation between molecular conformation and the spectra of the dimers are correct, the single substituent on the β-carbon of this dimer (V; R = R′ = H) provides insufficient hindrance to stabilise the protonated dimer (VI; R = R′ = H) so that the spectrum of the dimer closely resembles that of the parent monomer.

Preparations.—The interaction of the appropriate alkyl-lithium compound with Michler's ketone gave the α-ethyl, α-propyl, α-butyl, and α-isobutyl derivatives of Michler's Hydrol as compounds that crystallised from ethanol containing a trace of sodium hydroxide; in the absence of base, water is readily eliminated, yielding the olefin. Both the olefin and the alcohol are satisfactory precursors of the corresponding derivative of Michler's

[4] Evans, Jones, and Thomas, *J.*, 1955, 1824.

Hydrol Blue. The α-ethyl derivative was known,[5] and the α-methyl derivative could only be isolated as the known olefin.[6] The isopropyl derivative was obtained through the more easily prepared Grignard reagent, the product from which was isolated by treatment with aqueous ammonium chloride and therefore obtained as the olefin, m. p. 95—96°; Lemoult [7] gives m. p. 88°.

The α-t-butyl derivative, m. p. 149—150°, previously prepared through t-butylmagnesium chloride by Madelung and Völker [8] who give m. p. 147°, was obtained from *p*-dimethylaminophenyl-lithium and methyl pivalate, this method avoiding the difficult [9] preparation of t-butyl-lithium. The α-t-butyl derivative did not undergo rearrangement when heated with acid, in contrast to 2,2-dimethyl-1,1-diphenylpropan-1-ol.[10]

EXPERIMENTAL

1,1-*Bis*-(p-*dimethylaminophenyl*)*butan*-1-*ol*.—Propyl-lithium, from propyl bromide (6·15 g.) in ether, was added in nitrogen to Michler's ketone (2·7 g.) in ether and after 1 hr. the mixture was poured into water. The residue from the dried (Na_2SO_4) organic layer was twice crystallised from ethanol containing a trace of sodium hydroxide, giving the *hydroxy-compound* (2·7 g.), m. p. 111—112° (Found: C, 76·6; H, 8·8; N, 8·8. $C_{20}H_{28}N_2O$ requires C, 76·8; H, 9·0; N, 8·9%).

1,1-*Bis*-(p-*dimethylaminophenyl*)*pentan*-1-*ol*.—Butyl-lithium, from butyl bromide (6·85 g.), gave, by the aforementioned method, the *hydroxy-compound* (3·0 g.), m. p. 116—117° (Found: C, 77·2; H, 9·1; N, 8·3. $C_{21}H_{30}N_2O$ requires C, 77·2; H, 9·3; N, 8·6%).

1,1-*Bis*-(p-*dimethylaminophenyl*)-3-*methylbutan*-1-*ol*.—Isobutyl-lithium, from isobutyl bromide (6·85 g.), gave, by the aforementioned method, the *hydroxy-compound* (3·0 g.), m. p. 126—127° (Found: C, 77·6; H, 9·5; N, 8·5%).

1,1,3,3,-*Tetra*-(p-*dimethylaminophenyl*)*but*-1-*ene*.—1,1-Bis-(*p*-dimethylaminophenyl)ethylene (1·0 g.) in acetic acid (20 c.c.) was kept for 48 hr. and then poured into an excess of aqueous sodium hydroxide at 0°. The crystalline precipitate, twice crystallised from ethanol, gave the *base*, m. p. 174—176° (Found: C, 80·9; H, 8·0; N, 10·0. $C_{36}H_{44}N_4$ requires C, 81·2; H, 8·3; N, 10·5%).

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[5] Kohler and Patch, *J. Amer. Chem. Soc.*, 1916, **38**, 1210.
[6] Pfeiffer and Wizinger, *Annalen*, 1928, **461**, 152.
[7] Lemoult, *Compt. rend.*, 1911, **152**, 963.
[8] Madelung and Völker, *J. prakt. Chem.*, 1927, **115**, 40.
[9] Bartlett, Swain, and Woodward, *J. Amer. Chem. Soc.*, 1941, **63** 3229.
[10] Rogers, Brown, Rasmussan, and Heal, *J. Amer. Chem. Soc.*, 1953, **75**, 2991.