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SYNTHESIS AND ELECTRONIC ABSORPTION SPECTRA OF MONOETHYNOLOGS OF MALACHITE GREEN WITH p-SUBSTITUENT ON PHENYL RING[1)]

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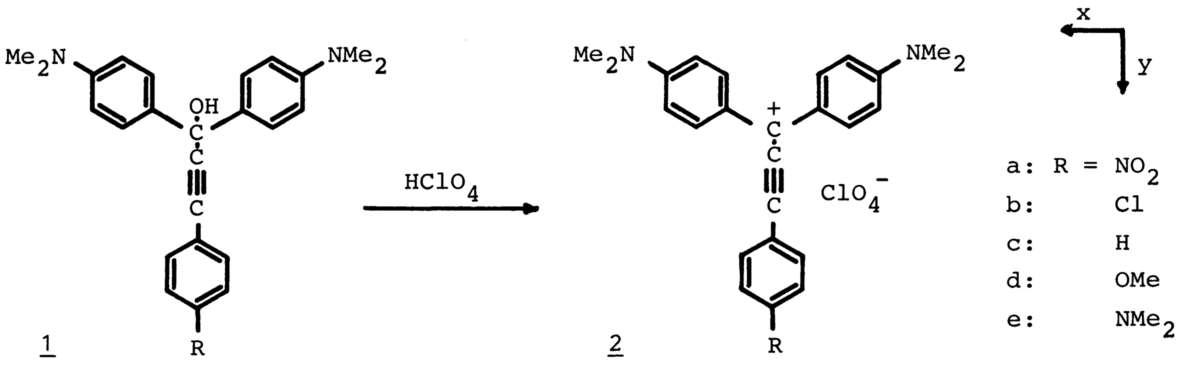
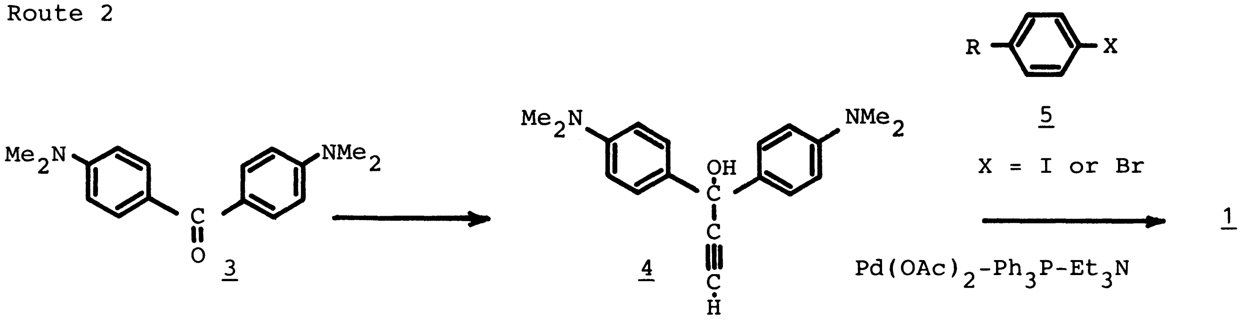
A series of bis(p-dimethylaminophenyl)(p-substituted phenylethynyl)carbonium perchlorates has been prepared. The electronic spectral properties are affected by both coplanarity of the cation parts and the effect of substituent on phenyl ring. A linear relationship was obtained between the wave numbers ($\tilde{\nu}$) of the longest wavelength absorption maxima and σ_p.

Introduction of an acetylenic bond into the resonating system of the triphenylmethane dyes makes the cation part coplanar and induces a great bathochromic effect on the peak in the visible region of the spectra.[2)] Thus, it is interesting to synthesize a series of bis(p-dimethylaminophenyl)-(p-substituted phenylethynyl)carbonium ions (2) (Scheme 1) and to examine the effect of substituents on their absorption spectra. We report herein the results of such investigations.



Scheme 1.

Route 2



The precursors 1 were prepared via two routes: 1) reaction of lithium p-substituted phenylacetylides with Michler's ketone (3), the method used in our previous paper (Route 1)$^{2)}$, and 2) ethynylation of 3 to the corresponding propynol 4 and subsequent palladium-catalyzed cross-coupling$^{3)}$ of 4 with p-substituted halogenobenzenes (5) (Route 2).$^{4)}$ Despite the low yields, Route 2 has advantage, because 5 is easily accessible and nitro compound (1a) can be prepared only by this route (Table 1). The yields of 1 by Route 2 seem to reflect the reactivity of 5. Treatment of 1 with perchloric acid (70%) in benzene gave 2 (Table 1).$^{5)}$

The absorption spectra of the series of 2 have been measured in CH_2Cl_2 (Fig. 1). These dyes except 2e show two well-defined absorption bands in the visible region. Assuming that the assignment of the bands in Malachite Green (MG) and its derivatives$^{6)}$ is applicable, the band A was assigned to the tran-

Table 1. Synthesis of 1 and 2 and absorption maxima of 2

	Yield of 1/%			Yield of 2/%	λ_{max}/nm (ε/$dm^3mol^{-1}cm^{-1}$)	
	Route 1	Route 2			B	A
1a	--	63	2a	94	494 (30100)	713 (81800)
1b	63[a)]	46	2b	38	498 (33600)	695 (90000)
1c	80	36	2c	68	493 (36200)	688 (101000)
1d	50	33	2d	45	530 (42600)	680 (103000)
1e	50	35	2e	83	---	663 (131000)

a) Potassium t-butoxide was used instead of BuLi.

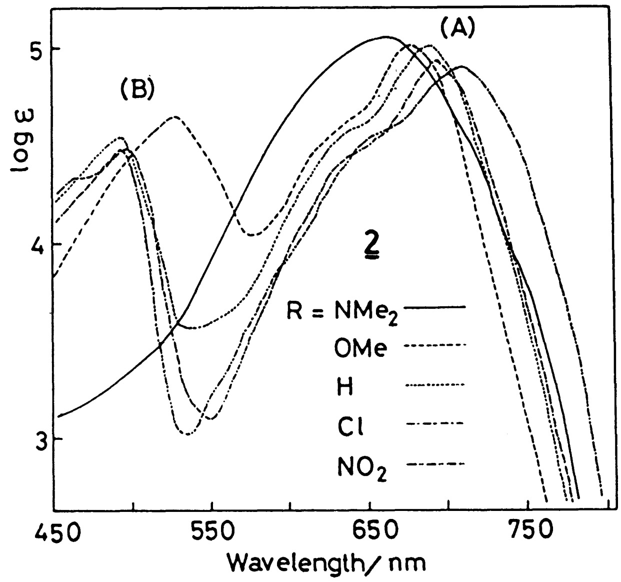


Fig. 1. Absorption spectra of 2 in CH_2Cl_2.

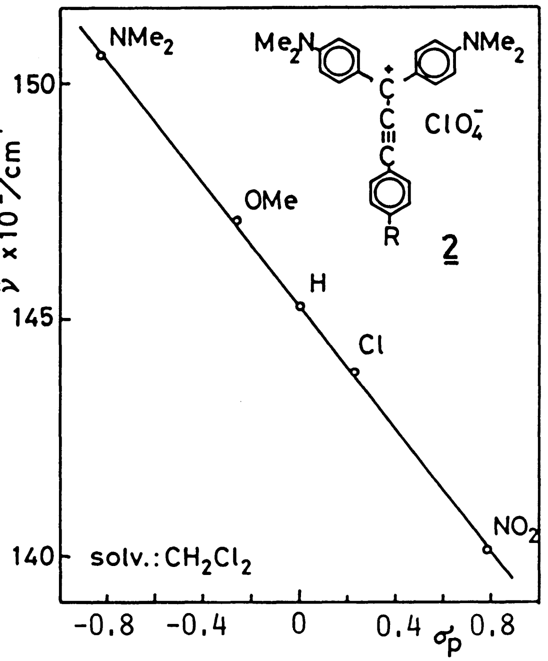


Fig. 2. Relation between σ_p and $\tilde{\nu}$ of 2.

sition polarized along the x-axis of 2 and the band B to that along the y-axis. The latter polarization is greatly enhanced by an electron-donating R, *e.g.*, OMe or NMe_2. Thus, the band B of 2d exhibits a red shift and that of 2e moves further and overlaps with the band A to give rise to an apparent intense single band. Characteristic shifts are also observed in the band A, which is shifted to longer wavelength, in the order NMe_2 < OMe < H < Cl < NO_2. The shifts in the wave numbers ($\tilde{\nu}$) of the band A are precisely proportional to the substituent constants (σ_p) evaluated by Brown7) (Fig. 2). This is in contrast to the trend in the MG derivatives reported by Barker *et al.*:8) a plot of $\tilde{\nu}$ (band A) of the corresponding p-substituted compounds and the substituent constant σ_p deviates greatly from linearity.

From these results, the spectral behaviors of 2 seem to reflect that the introduction of an acetylenic bond releases steric congestion between *ortho*-hydrogen atoms of the phenyl groups in the triphenylmethane dyes and the effect of the substituents is subsequently exerted on the whole of the dye system.

On the basis of the present findings, we can design and develop new triphenylmethane dye ethynologs such as $R\text{-}C{\equiv}C\text{-}C_6H_4\text{-}p\text{-}NMe_2$ [R = $p\text{-}Me_2NC_6H_4(C_6H_5)\text{-}C^+$, 9-xanthenylium, 9-thioxanthenylium, and the like], which absorb intensively near-infrared light at 700 - 800 nm.9) Studies on the near-infrared dyes are further in progress.

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4) A typical example of Route 2: Treatment of 3 (2.00 g, 7.5 mmol) in dry THF (50 ml) with lithium acetylide-ethylenediamine complex (3.5 g, 38 mmol) at 0 °C for 90 min gave 4 (2.10 g, 95%).[5)] A mixture of 4 (0.25 g, 0.85 mmol), 5a(R = NO_2, X = I) (0.21 g, 0.85 mmol), $Pd(OAc)_2$ (15 mg, 0.07 mmol), and Ph_3P (29 mg, 0.11 mmol) was refluxed in triethylamine (50 ml) for 3 h. Work-up in the standard manner gave 1a (0.22 g, 63% after recrystallization from MeOH - Et_2O).[5)]

5) All products gave satisfactory elemental analyses and spectral data (IR, ^1H-NMR, and MS). Mp (°C): 1a, 103 - 105; 1b, 106 - 108; 1c, 163 - 164; 1d, 117; 1e, 143 - 145; 2a, ca. 225 (dec.); 2b, ca. 230 (dec.); 2c, 189 (dec.); 2d, 232 - 235; 2e, ca. 240 (dec.).

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