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ETHYNOLOGS OF TRIPHENYLMETHANE DYES. SYNTHESES AND PROPERTIES OF ACETYLENIC ANALOGS OF MALACHITE GREEN, CRYSTAL VIOLET, AND THEIR RELATED COMPOUNDS

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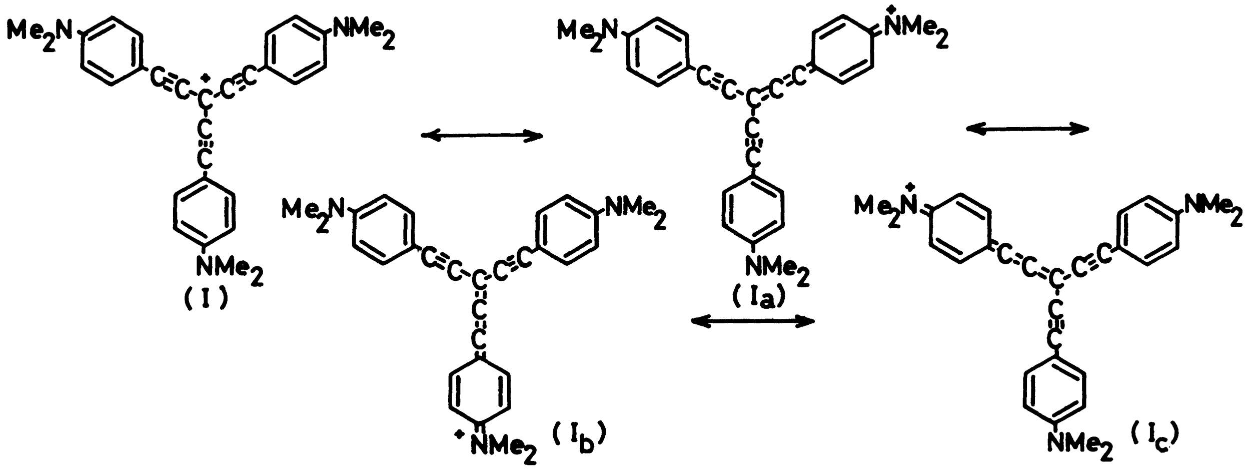
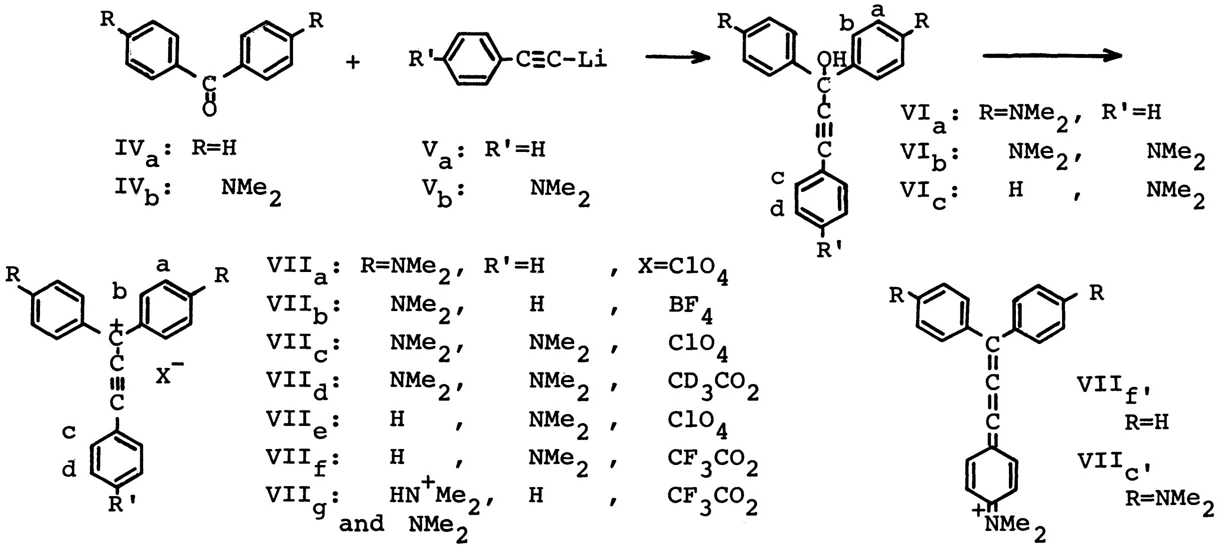
The acetylenic analogs of malachite green, crystal violet, and their related compounds have been synthesized to examine an effect of an acetylenic bond on a dye system.

Triphenylmethane dyes are a well known and important class of synthetic coloring matters, in which two of the most useful are malachite green (II) and crystal violet (III). The series of an ethynolog of triaryl carbenium ion with *p*-dimethylamino substituent, *e.g.*, (I) can typically be a completely planar analog of III, in which an acetylenic bond is inserted between the central carbon atom and aryl group. In these dye ethynologs$^{1)}$ an appearance of a new resonance system containing an allene-quinoid structure is expected by delocalization of a positive charge. Especially the cation (I) should be fully stabilized by contribution of the three canonical forms (I_a, I_b, and I_c) of the immonium type. Thus, it seemed quite interesting to prepare the series of compounds and compare their properties with those of the classical triphenylmethane dyes. We wish to report the first syntheses and properties of the ethynologs (VII_{a-g}) of II, III, and their related compounds.$^{2)}$

Treatment of the ketone (IV) with the lithium acetylide (V) in THF at 0°C gave VI_a [white needles, mp 163-164°C, 80%, IR (KBr-disk): 3100-3200 (OH), 2200 (C≡C) cm^{-1}; UV: λ_{max}^{THF} nm (log ε) 257 (4.88), 269 (4.87); ^{1}H NMR (CDCl$_3$): δ 7.59-7.45 (2H, m, H^c), 7.48 (4H, J_{ab}=9, H^a), 7.32-7.24 (3H, m, H^d and R'), 6.69 (4H, J_{ab}=9, H^b), 2.93 (12H, s, R), 2.64 (1H, s, OH)], VI_b [white needles, mp


(I)
(Ia)
(I_b)
(I_c)



IV_a: R=H

IV_b: NMe_2

V_a: R'=H

V_b: NMe_2

VI_a: R=NMe_2, R'=H

VI_b: NMe_2, NMe_2

VI_c: H, NMe_2

	R	R'	X
VII_a:	R=NMe_2,	R'=H,	X=ClO_4
VII_b:	NMe_2,	H,	BF_4
VII_c:	NMe_2,	NMe_2,	ClO_4
VII_d:	NMe_2,	NMe_2,	CD_3CO_2
VII_e:	H,	NMe_2,	ClO_4
VII_f:	H,	NMe_2,	CF_3CO_2
VII_g:	HN^+Me_2, and NMe_2	H,	CF_3CO_2

$VII_{f'}$, R=H

$VII_{c'}$, R=NMe_2

143-145°C, 50%, IR (KBr-disk): 3200 (OH), 2200 (C≡C) cm^{-1}; UV: λ_{max}^{THF} nm (log ε) 271 (4.64), 288 (4.64), ^1H NMR (CD_2Cl_2): δ 7.43 (4H, J_{ab}=9, H^b), 7.33 (2H, J_{cd}=9, H^c), 6.67 (4H, J_{ab}=9, H^a), 6.64 (2H, J_{cd}=9, H^d), 2.96 (6H, s, R'), 2.91 (12H, s, R), 2.71 (1H, s, OH)], and VI_c [white needles, mp 148-149°C, 89%, IR (KBr-disk): 3500 (OH), 2200 (C≡C) cm^{-1}; UV: λ_{max}^{THF} nm (log ε) 293 (4.55); ^1H NMR (CD_2Cl_2): δ 7.54-7.73 (4H, m, H^b), 7.20-7.46 (6H, m, H^a and R), 7.36 (2H, J_{cd}=8, H^c), 6.64 (2H, J_{cd} =8, H^d), 2.97 (6H, s, R'), 2.93 (1H, s, OH), respectively.[3] A solution of the alkynyl alcohols (VI_{a-c}) in benzene was mixed with corresponding strong acids to yield deeply colored stable crystals VII_a [deep green needles, mp 189°C (dec.), 68%, (m/e): 353 (M^+- ClO_4^-); IR (KBr-disk): 2180 (C≡C) cm^{-1}], VII_b [deep green needles, mp 175-178°C (dec.), 61%, Mass (m/e): 353 (M^+- BF_4^-); IR (KBr-disk): 2180 (C≡C) cm^{-1}], VII_c [brilliant deep green leaflets, mp *ca.*240°C (dec.), 83%, Mass (m/e): 396 (M^+- ClO_4^-); IR (KBr-disk): 2140 (C≡C) cm^{-1}], respectively. Some attempts have been made to prepare VII_e as pure crystals by the same manner from VI_c; these have failed because of unstability of VII_e. However, VII_f[4] could be generated by dissolving VI_c into a solution of CF_3CO_2D-CD_2Cl_2 at -50°C giving rise to intense deep blue solution of which the NMR and electronic spectra were definitely measured. The spectra of a red solution resulted from dissolving VI_a into trifluoroacetic acid were also taken to show VII_g, in which a proton was assumed to exchange between two dimethylamino groups. The spectral parameters of these new dyes are summarized with related compounds in Table 1-2. Examining Tables the following trends can be noted. (1) The spectra (NMR of VII_{a-b} and VII_{c-d}, and electronic spectra of VII_{a-b}) are almost independent of anion species. (2) The changes in the chemical shift (Δδ) of dimethylamino group when the alcohol is converted into the cation are -0.53 [VI_a→VII_a], -0.39 (R) and -0.18 (R') [VI_b→VII_d], -0.57 [VI_c→VII_f], and -0.72 [VI_a→VII_g] ppm, respectively. The signals of R', H^c, and H^d of VII_f show downfield shifts from those of VII_c and VII_d, namely, Δδ = 0.28∿0.30, 0.19∿0.20, and 0.33∿0.34 ppm. These demonstrate that the positive charge density on the charged carbon decreases and considerably moves to the nitrogen atom in VII_f. Consequently the contribution of allene-quinoid structure ($VII_{f'}$) is not likely to be negligible. On the other hand, Michler's hydrol system [p-$Me_2NC_6H_4$-$\overset{+}{\underset{|}{C}}$-$C_6H_4$-$p$-$NMe_2$] predominates exclusively in VII_{a-d} similar to II and III. The situation described above becomes more apparent from their electronic spectral behavior (Table 2 and Scheme). (3) Addition of ethynyl group to the classical dye system resulted effectively in a shift of λ_{max} of the longest wavelength to much longer [triphenyl carbenium ion (IX)→(VIII, *i.e.*,VII: R=R'=H): 73, II→VII_a: 67, and III→VII_c: 79 nm]. (4) It is noteworthy that introduction of dimethylamino group into p-position of

Table 1. NMR Parameters and Assignments of Cations (ppm, Relative to Internal TMS)

Compound	R	H^a (J_{ab})	H^b (J_{ab})	H^c (J_{cd})	H^d (J_{cd})	R'	Solvent (°C)
VII_a	3.47 s	7.19 (9.5 Hz)	8.07 (9.5 Hz)	7.77 $\sim$ 7.88 m	7.54 $\sim$ 7.76 m		$(CD_3)_2CO$ (35)
VII_b	3.46 s	7.19 (9.5 Hz)	8.06 (9.5 Hz)	7.78 $\sim$ 7.88 m	7.55 $\sim$ 7.76 m		$(CD_3)_2CO$ (35)
VII_c	3.30 s	6.91 (9.5 Hz)	7.90 (9.5 Hz)	7.62 (9.0 Hz)	6.77 (9.0 Hz)	3.14 s	$CDCl_3$ (35)
VII_d	3.31 s	6.92 (9.5 Hz)	7.91 (9.5 Hz)	7.63 (9.0 Hz)	6.77 (9.0 Hz)	3.16 s	CD_3CO_2D-CD_2Cl_2* (1:3) (-10)
VII_f	7.38 $\sim$ 7.92 m			7.82 (9.0 Hz)	7.11 (9.0 Hz)	3.54 s	10% CF_3CO_2D in CD_2Cl_2*(-30)
VII_g	3.65 s	7.60 (8.9 Hz)	8.07 (8.9 Hz)	7.51 $\sim$ 7.75 m			CF_3CO_2D* (35)
II	3.33 s	6.94 (9.5 Hz)	7.41 (9.5 Hz)	7.12 $\sim$ 7.84 m			CD_2Cl_2 (35)
III	3.22 s	6.85 (10.0 Hz)	7.35 (10.0 Hz)				CD_2Cl_2 (35)

* measured for the cations generated by dissolving the corresponding alkynyl alcohols into the solvent system.

Table 2. Electronic Spectra of Cations

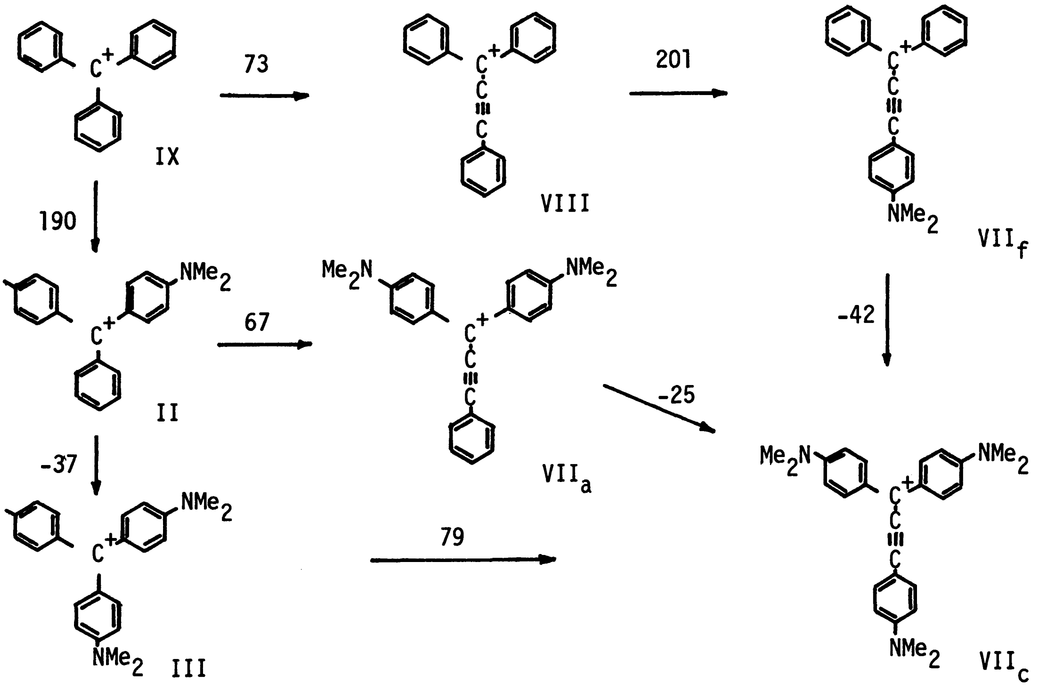
Compound	VII_a	VII_b	VII_c	VII_f
λ_{max} nm (log ε)	492 (4.56) 688 (5.00)	492 (4.58) 688 (5.01)	633 (5.12)	401 (4.10) 630 (4.57) 705 (4.59)
Solvent	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	1% CF_3CO_2H in CH_2Cl_2 (-70°C)

VII_g	II[5]	III	VIII[1c,d]	IX[7]
495 (4.68)	428 (4.30) 621 (5.17)	584 (5.08)	449 (4.43) 504 (4.57)	405 (4.59) 431 (4.60)
CF_3CO_2H	98% CH_3CO_2H	CH_2Cl_2	FSO_3H-SbF_5 (-65°C)	98% H_2SO_4

phenyl group in VIII gives rise to an enormous red shift ($VIII \rightarrow VII_f$: $\Delta\lambda$= 201 nm), which may suggest favorable evidence for the existence of the allene-quinoid structure ($VII_{f'}$). Contrary to this a blue shift ($\Delta\lambda$= -25 nm) is observed from VII_a to VII_c, in which apparently the chromophore p-Me_2N-$C_6H_4C\equiv C$-$\underset{|}{\overset{+}{C}}$-$C_6H_4$-$p$-$NMe_2$ is not so much effective as Michler's hydrol system because $VII_{c'}$ derived by delocalization of the positive charge is probably energetically unfavorable.

Further investigation elucidating evidently the allene-quinoid structure by synthesis of (I) with its related compounds is now in progress.

Scheme Shifts [Δλ (nm)] of the Longest Wavelength Absorption Maxima



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References and Notes

1) For references on alkynyl cations relating to this work, see, a) H. G. Richey, Jr., J. C. Philips, and L. E. Rennick, *J. Am. Chem. Soc.*, 87, 1381 (1965); H. G. Richey, Jr., L. E. Rennick, A. S. Kushner, J. M. Richey, and J. C. Philips, *ibid.*, 87, 4017 (1965); b) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, 87, 5632 (1965); c) G. A. Olah, C. U. Pittman, Jr., R. Waak, and M. Doran, *ibid.*, 88, 1488 (1966); d) G. A. Olah and P. von R. Schleyer, eds. (1968), "Carbonium Ions", Vol. I, Wiley (Interscience), New York; e) G. A. Olah, R. J. Spear, P. W. Westerman, and J-M. Denis, *J. Am. Chem. Soc.*, 96, 5855 (1974); f) J. D. Mee, *ibid.*, 96, 4712 (1974); *idem.*, *J. Org. Chem.*, 42, 1035 (1977); J. D. Mee and D. M. Strumer, *ibid.*, 42, 1041 (1977).

2) For our previous studies on the linear conjugated systems, see, M. Nakagawa, S. Akiyama, K. Nakasuji, and K. Nishimoto, *Tetrahedron*, 27, 5041 (1971); S. Akiyama, Y. Takeuchi, A. Yasuhara, M. Nakagawa, and K. Nishimoto, *Bull. Chem. Soc. Jpn.*, 46, 2830 (1973), and references cited therein.

3) All new crystalline compounds described in this paper gave IR, NMR, and mass spectral data consistent with the assigned structures and satisfactory elemental analyses were obtained.

4) In the NMR measurement of VII$_f$ increasing temperature gradually resulted in a spectral change at -30∿+10°C. After the completion of the change, the acid solution was drowned with excess sodium carbonate and the mixture was worked up to give 1,1-dipphenyl-2-(*p*-dimethylaminobenzoyl)-ethylene [mp 170-172°C].[3)]

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