Tetrahedron Letters,Vol.25,No.45,pp 5143-5146,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

SYNTHESIS OF PYRYLIUM SALTS FROM TRISUBSTITUTED 1,4-PENTADIYN-3-OLS WITH $HClO_4$(1)

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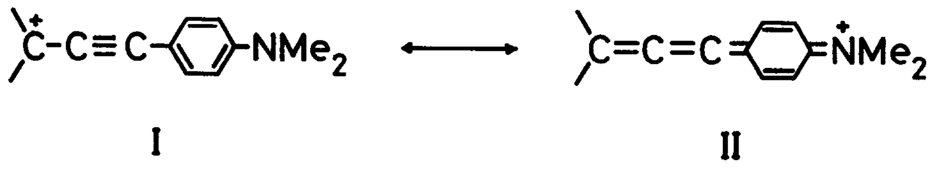
Summary: The synthesis of 2,4,6-trisubstituted pyrylium salts from 1,3,5-trisubstituted 1,4-pentadiyn-3-ols with $HClO_4$ is reported for the first time.

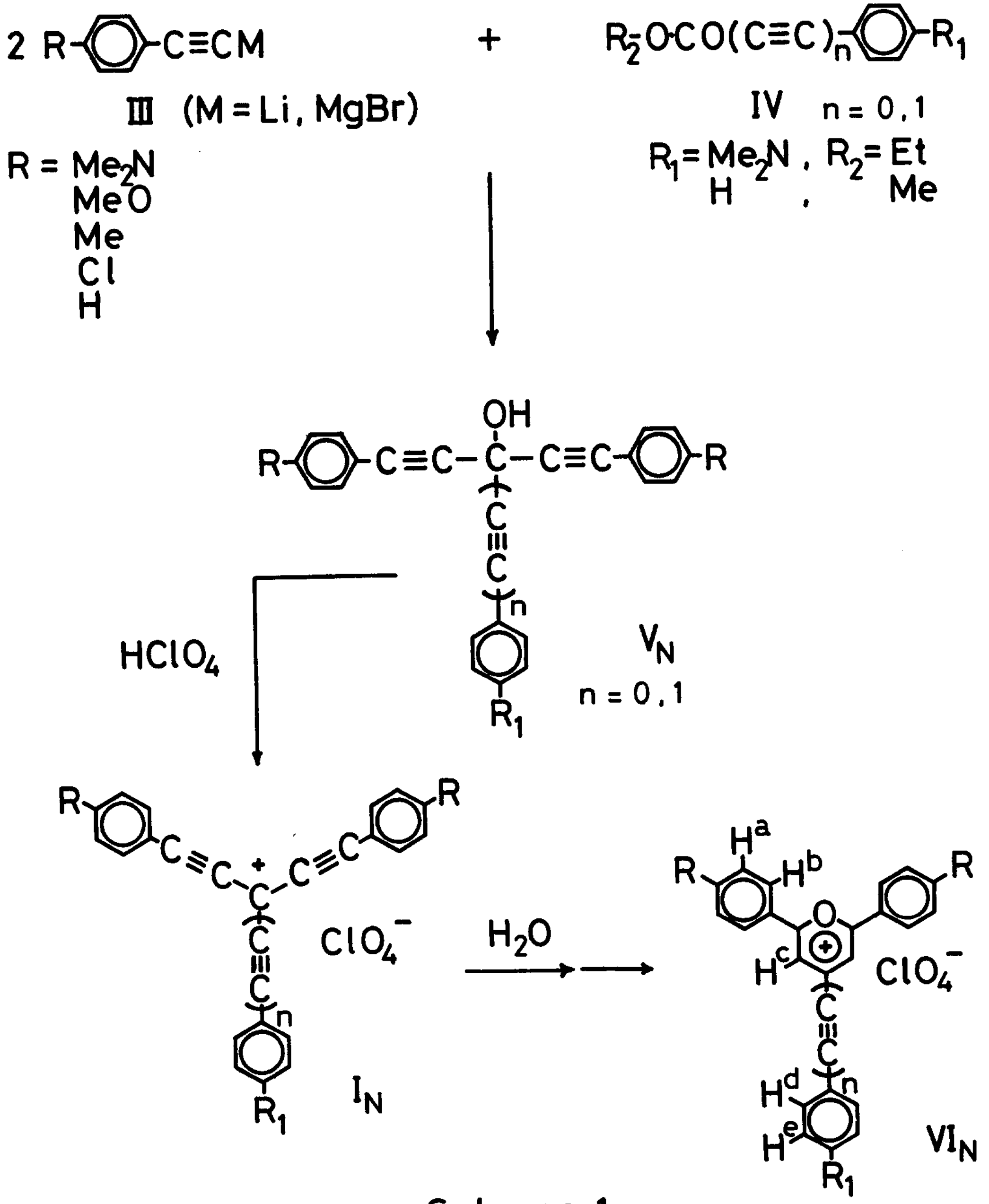
Throughout the study on the monoethynologs(1,2) of Malachite Green, Crystal Violet, and their related compounds, the synthesis of bis- and tris-ethynologs (I_N) of the above dyes has been the focus of considerable interest. These ethynologs may be expected to form a new resonance system (I ↔ II) containing an allene-quinoid structure (II) realized by delocalization of a positive charge. Then, the alcohols (V_N) were prepared for the precursors of I_N and treated with $HClO_4$. However, it was found that the pyrylium salts (VI_N) were obtained in moderate yields instead of the anticipated ethynologs (I_N) (Scheme 1).

In this communication, we wish to report a novel synthesis of 2,4,6-trisubstituted pyrylium salts (VI_N) from 1,3,5-trisubstituted 1,4-pentadiyn-3-ols (V_N) by trearment with $HClO_4$.

Reaction of the *p*-substituted phenylacetylides (III)(3) (2 mol) with the corresponding esters (IV) [*e.g.*, methyl *p*-dimethylaminobenzoate or ethyl *p*-dimethylaminophenylpropiolate(3)] (1 mol) in THF at -78 °C gave V_N as depicted in Scheme 1.(4)



Treatment of V_N with $HClO_4$ (70 wt%) in benzene – EtOH (2 : 1, vol) yielded VI_N (Table 1). In Table 1, VI_3, VI_4, and VI_7 are new compounds, whose structures were clearly assigned from the data obtained.[4,5] The other pyrylium salts were identified distinctly by comparing their physical data with those of the literature or/and the authentic samples prepared according to the conventional methods.[6,7]



Scheme 1.

Table 1. Synthesis of Pyrylium Salts (VI_N) from Alcohols (V_N)

N	n	R	R_1	V_N	VI_N	mp (°C)	yield (%)
1	0	Me_2N	H	V_1	VI_1	264 – 266[a]	67
2	0	MeO	H	V_2	VI_2	*ca.* 275[b]	89
3	0	Me	H	V_3	VI_3	278 – 279	79
4	0	Cl	H	V_4	VI_4	293 – 295	52
5	0	H	H	V_5	VI_5	289 – 292[c]	32[d]
6	1	H	H	V_6	VI_6	179 – 181[e]	68
7	1	Me_2N	Me_2N	V_7	VI_7	*ca.* 230	59

a) Reference 7): 264 – 265 °C.
b) Reference 7): 274 – 275 °C.
c) J. A. VanAllen and G. A. Reynolds, J. Org. Chem., 33, 1102 (1968): 293 – 295 °C.
d) Based on crude V_5.
e) J. J. Doney, C. H. Chen, and H. R. Luss, Tetrahedron Lett., 23, 1747 (1982): 179 – 181 °C.

The formation of the pyrylium salts (VI_N) may be presumed as follows: In the acidic medium the alcohols (V_N) give the labile cations (I_N),[8] which undergo rapidly Meyer-Schuster rearrangement[9] and then yield a series of compounds, *e.g.*, 2-pentene-1,5-dione, 2-penten-4-yn-1-one derivatives or/and their enols, by an addition of water.[10] Subsequently, a pyrylium ring is yielded as a result of intramolecular condensation and succeeding aromatization reactions.

Interestingly, the effect of the substituents (R) was observed in this pyrylium ring formation reaction. The alcohols (V_3, V_4, and V_7) bearing strong electron donating groups cyclized quite easily to the corresponding pyrylium salts at room temperature. However, the others needed heating for several hours to complete the above reactions. From these results, the order of the ease of the cyclization was as given follows: $Me_2N > MeO > Me > H \approx Cl$

Acknowledgement: The authors wish to thank Professor Emeritus Masazumi Nakagawa and Professor Ichiro Murata of Osaka University for their kind advice and valuable discussion. The authors are also indebted to Dr. Akio Yasuhara of National Institute for Enviornmental Studies of Japan for measuring ^1H NMR and mass spectra. This research has been supported in part by a Grant-in-Aid for Scientific Research (Nos. 56470022 and 58470031) from the Ministry of Education of Japan, which is gratefully acknowledged.

References and Notes

1) Ethynologs of Triphenylmethane Dyes. Part II. For Part I, see S. Akiyama, K. Yoshida, M. Hayashida, K. Nakashima, S. Nakatsuji, and M. Iyoda, Chem. Lett., 1981, 311.
2) S. Akiyama, K. Nakashima, S. Nakatsuji, M. Hamada, and Y. Izaki, Bull. Chem. Soc. Jpn., 56, 947 (1983).
3) S. Akiyama, S. Nakatsuji, K. Yoshida, K. Nakashima, T. Hagiwara, H. Tsuruta, and T. Yoshida, Bull. Chem. Soc. Jpn., 56, 361 (1983).
4) The IR, ^{1}H NMR, and mass spectral data of all crystalline compounds described in this communication are consistent with the assigned structures. Acceptable combustion data were also obtained.
5) Spectral data of the new compounds (VI_3, VI_4, and VI_7): VI_3, red crystals, IR (Nujol) 1615 cm^{-1}; UV (CH_2Cl_2) 373 (ε 40700), 445 (30100), and 532 nm (3580); ^{1}H NMR (DMSO-d_6) δ 2.55 (6H, s, Me), 7.21 – 7.46 and 7.74 – 8.00 (3H, m, H^e and R_1 = H), 7.62 (4H, d, J = 9 Hz, H^a), 8.46 – 8.57 (2H, m, H^d), 8.52 (4H, d, J = 9 Hz, H^b), and 9.06 (2H, s, H^c); VI_4, yellow crystals, IR (Nujol) 1620 cm^{-1}; UV (CH_2Cl_2) 303 (ε 7470), 377 (14100), and 432 nm (9330); ^{1}H NMR (DMSO-d_6) δ 7.71 – 7.88 and 8.52 – 8.63 (13H, m, aromatic protons) and 9.13 (2H, s, H^c); VI_7, deep violet crystals, IR (KBr) 2170 and 1570 cm^{-1}; UV (CH_2Cl_2) 590 (ε 76600) and 640 nm (63000); ^{1}H NMR (DMSO-d_6) δ 3.07 (6H, s, Me_2N), 3.15 (12H, s, Me_2N), 6.84 (2H, d, J = 9 Hz, H^e), 6.92 (4H, d, J = 9.5 Hz, H^a), 7.55 (2H, d, J = 9 Hz, H^d), 8.00 (2H, s, H^c), and 8.11 (4H, d, J = 9.5 Hz, H^b).
6) For a review of pyrylium salts, see A. T. Balaban, G. W. Fischer, A. Dinculescu, A. V. Koblik, G. N. Dorofeenko, V.V. Mezheritskii, and W. Schroth, "Pyrylium Salts: Syntheses, Reactions, and Physical Properties," in "Avdances in Heterocyclic Chemistry, Supplement 2," ed by A. R. Katritzky, Academic Press, New York (1982).
7) *E.g.*, for VI_6, *cf.* R. Wizinger, S. Losinger, and P. Ulrich, Helv. Chim. Acta, 39, 5 (1956).
8) Attempts to characterize the cations (I_N) by the ^{1}H NMR measurements of V_N in various anhydrous acidic media (CF_3CO_2D, CD_3CO_2D, and $FSO_3H - SbF_5$) at -30 – -70 °C have been so far impossible.
9) H. Krauch and W. Kunz, "Organic Name Reactions," John Wiley & Sons, Inc., New York (1964) p. 313, and references cited therein.
10) In the study on the monoethynologs of triphenylmethane dyes,[1)] we have isolated the ketone, 1,1-diphenyl-2-(*p*-dimethylaminobenzoyl)ethylene, which was obtained by the treatment of 3-(*p*-dimethylaminophenyl)-1,1-diphenyl-2-propyn-1-ol with CF_3CO_2H, followed by neutralization with aqueous Na_2CO_3.

(Received in Japan 16 July 1984)