A Simple and Convenient Synthesis of Aryl-Substituted Push-Pull Butadienes from 1,1-Diaryl-2-propyn-1-ols[1)]

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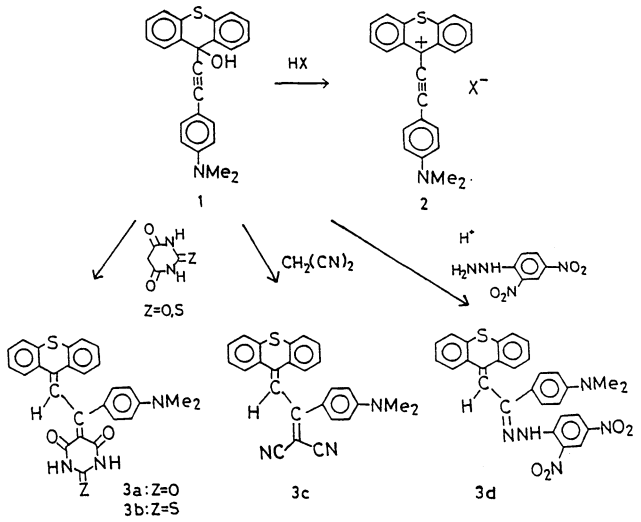
Synopsis. 1,1-Diaryl-2-propyn-1-ol derivatives reacted with several nucleophiles to afford novel 1,1-diarylbutadiene systems. An efficient one-step synthesis of aryl-substituted push-pull butadiene systems was achieved by this reaction.

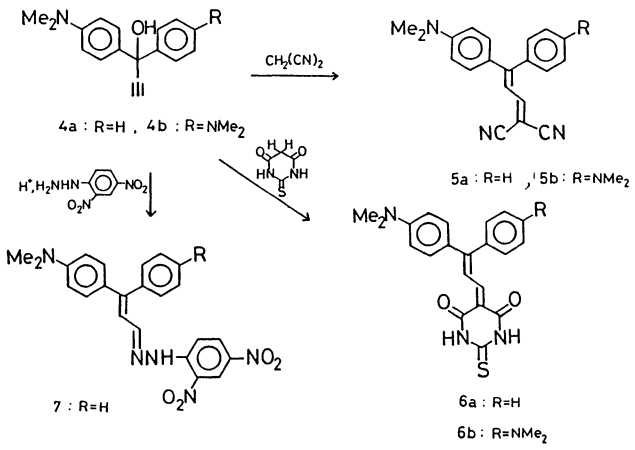
Push-pull butadienes bearing an electron-donor on one end and an electron-acceptor on the other end of the molecule are one of the fundamental π-electron systems in merocyanine dyes.[2)] Recently, special interest regarding such π-electron systems is focused on their potential applicability to non-linear optics.[3)] Moreover, the systems are useful building blocks for the formation of cyclic systems by a Diels-Alder reaction.[4)]

In this paper, we wish to report on a new method for the synthesis of such butadienes, which have been found in the course of our studies on the new xanthenylium dye ethynologs **2**, possible near infrared dyes for the optical and laser data-storage technology.[5)]

Treatment of acetylenic alcohol **1** at room temperature with inorganic acids (e.g., $HClO_4$, HBF_4, etc.) or various organic acids (e.g., picric acid, *p*-TsOH, etc.) gave the mono-cationic salt **2**, as shown in Scheme 1.[5)] On the contrary, the reaction of **1** with thiobarbituric acid gave no cationic salt and resulted in the formation of reddish crystals (80%) with an absorption maximum at 588 nm (CH_2Cl_2). The spectroscopic investigations (IR, ^1H NMR, and MS), as well as elemental analyses, showed that the compound obtained was a new 1,3-butadiene derivative (**3b**).[6)] It was apparent from the result that the acidity of thiobarbituric acid was sufficiently strong to remove the hydroxyl group of **1** and the nucleophilicity of the conjugated base was sufficient to attack the terminal carbon (i.e., C_3) of the triple bond. Analogous reactions of **1** with barbituric acid, malononitrile, and 2,4-dinitrophenylhydrazine[7)]



Scheme 1.

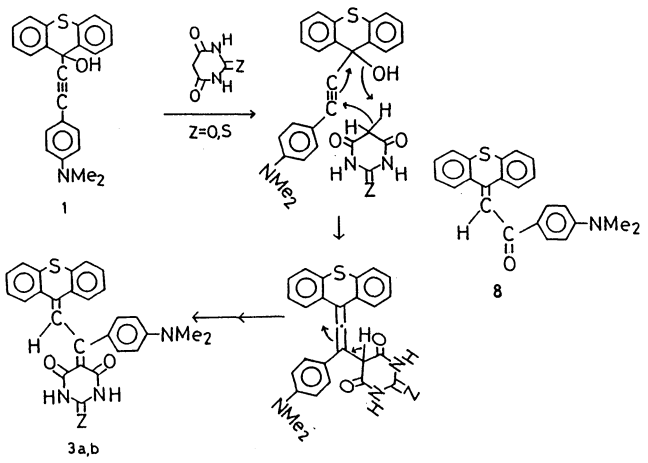


Scheme 2.

Table 1. Yields, Melting Points, Analytical Data, and Electronic Spectra of **3**, **5**, **6**, and **7**

Compound	Yield[a)] %	Mp θ_m/°C	Molecular formula	Found (Calcd) C(%)	H(%)	N(%)	UV[d)] λ_{max}/nm ($\varepsilon\times10^{-4}$)
3a	81	>300	$C_{27}H_{21}N_3O_3$	69.17(69.36)	4.75(4.53)	8.81(8.99)	557(1.53)
3b	80	>300	$C_{27}H_{21}N_3O_2S_2$	67.06(67.06)	4.55(4.38)	8.54(8.69)	588(1.19)
3c	62	214—216	$C_{26}H_{19}N_3S$	76.89(77.01)	4.93(4.72)	10.21(10.36)	447(2.22)
3d	79	ca. 230[b)]	$C_{29}H_{23}N_5O_4S$	64.62(64.80)	4.45(4.31)	12.91(13.03)	446(2.28)
5a	83	79—80	$C_{20}H_{17}N_3$	80.45(80.24)	5.83(5.72)	14.00(14.04)	496(3.69)
5b	85	136—137	$C_{22}H_{22}N_4$	76.72(77.16)	6.66(6.48)	16.13(16.36)	498(3.32)
6a	92	ca. 279[b)]	$C_{21}H_{19}N_3O_2S$	66.55(66.82)	4.85(5.07)	10.90(11.13)	595(7.88)
6b	86	ca. 250[b)]	$C_{23}H_{24}N_4O_2S$	63.22(62.99)	5.84(5.98)	12.64(12.78)[c)]	595(8.06)
7	82	ca. 215[b)]	$C_{23}H_{21}N_5O_4$	63.82(64.03)	4.99(4.91)	16.09(16.23)	496(3.96)

a) Yield of isolated product. b) Decomposition point. c) $C_{23}H_{24}N_4O_2S\cdot H_2O$. d) The longest wavelength band (solvent CH_2Cl_2).



Scheme 3.

afforded **3a**, **3c**, and **3d** in 81, 62, and 79%, respectively (Scheme 1, Table 1).

As an extension of the reaction using acetylenic alcohol **1**, we have tried such reactions as shown in Scheme 2, using acetylenic alcohols **4a**, **4b** prepared by the ethynylation of the corresponding ketones.

The reaction with barbituric acid or thiobarbituric acid (**4**→**6**) could proceed readily, even at room temperature, in good yields. In the case of malononitrile (**4**→**5**), however, appropriate heating was necessary. The acid-catalyzed reaction with 2,4-dinitrophenylhydrazine (**4**→**7**) occurred readily in good yield.

A sort of acid-catalyzed propargylic rearrangement[8] would participate in the reactions and a plausible process of the formation of **3** is shown above (Scheme 3). No reaction of thiobarbituric acid with the ketone **8**[9] occurred under the same conditions and the starting materials were recovered. Therefore, the formation of the ketone as an intermediate in the reaction might be ruled out.

In conclusion, this simple, efficient method provides a new practical way to obtain push-pull type diene systems having potential applicability to dye chemistry and to synthetic chemistry as well.

Experimental

Melting points were uncorrected. IR spectra were obtained on Shimadzu IR 408 and JASCO IRA 810 spectrophotometers. ^{1}H NMR spectra were measured on a JEOL JNM-FX 90Q instrument and the chemical shifts are given in δ-values with respect to TMS used as an internal standard. UV spectra were obtained on a Hitachi 200-10 spectrophotometer. MS spectra were taken using a JEOL JMS-DX303 mass spectrometer.

The syntheses and some physical properties of acetylenic alcohol **1** and cationic salts **2** were partly reported in Ref. 5.

The Syntheses of Acetylenic Alcohol 4a and 4b: To a chilled solution (−10 °C) of 4-dimethylaminobenzophenone (2.0 g, 8.8 mmol) in abs. tetrahydrofuran (100 ml) was bubbled acetylene gas to be saturated. After 10 min, a lithium acetylide-ethylenediamine complex (6.1 g, 67 mmol) was added. The reaction mixture was stirred for 1.5 h at the same temperature and then for 1.5 h at ambient temperature, and poured into H_2O (100 ml). After separation and extraction of the water layer with benzene (100 ml, and then 50 ml), the combined organic layer was washed with brine (150 ml), dried over $MgSO_4$, and evaporated in vacuo. The crude solid obtained was recrystallized with ether to give 1.8 g (78%) of pure **4a** as colorless crystals: mp 121—122 °C; IR (Nujol) ca. 3300 (OH), 3270 (C≡CH), 2110 (C≡C), and 1610 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=2.75 (1H, s, OH), 2.82 (1H, s, C≡CH), 2.92 (6H, s, NMe_2), 6.62 (2H, d, J=9 Hz), 7.22—7.75 (5H, m, aromatic H); EI-MS m/z 251 (M^+). Found: C, 81.31; H, 6.77; N, 5.47%. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57%. By the same method as above, **4b** was prepared in 95% yield; mp 154—155 °C: IR (Nujol) ca. 3300 (OH), 3250 (C≡CH), 2110 (C≡C), and 1610 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=2.80 (1H, s, C≡CH), 2.93 (12H, s, NMe_2), 3.05 (1H, s, OH), 6.63 (4H, d, J=9 Hz, aromatic H), 7.40 (4H, d, J=9 Hz, aromatic H); EI-MS m/z 294 (M^+). Found: C, 77.18; H, 7.64; N, 9.41%. Calcd for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52%.

Reactions of Acetylenic Alcohols 1, 4a, and 4b with Barbituric or Thiobarbituric Acid; General Procedure: Acetylenic alcohol **1** (80 mg, 0.22 mmol) in MeOH (20 ml) was mixed with thiobarbituric acid (32 mg, 0.22 mmol) in MeOH (20 ml) at room temperature. The color of the solution turned immediately from pale yellow to deep bluish-violet. After stirring for 1 h, the mixture was concentrated to give precipitates, which were filtered and then washed with ether. The resulting dark-red crystals (82 mg, 80%) were recrystallized with CH_2Cl_2-ether for an analytical sample: mp>300 °C; IR (Nujol) 3175 (NH), 1690, 1650 (C=O), and 1600 cm^{-1} (C=C); ^{1}H NMR (DMSO-d_6) δ=2.88 (6H, s, NMe_2), 6.29 (2H, J=9 Hz, aromatic H), 7.18 (2H, d, J=9 Hz, aromatic H), 7.14—7.42 (9H, m, aromatic and olefinic H), 11.83 (1H, s, NH); FAB-MS m/z 484 (M+1). By the same method as above **3a**, **6a**, **6b** were prepared from **1**, **4a** or **4b**; **3a**: dark-reddish violet crystals; IR (Nujol) 3200 (NH), 1720, 1690, 1665 (C=O), and 1600 cm^{-1} (C=C); ^{1}H NMR (DMSO-d_6) δ=2.88 (6H, s, NMe_2), 6.27 (2H, d, J=9 Hz, aromatic H), 7.12 (2H, d, J=9 Hz, aromatic H), 7.08—7.43 (9H, m, aromatic and olefinic H), 10.74 (1H, s, NH); FAB-MS m/z 468 (M+1). **6a**: yellowish green crystals; IR (Nujol) 3150 (NH), 1690, 1640 (C=O), and 1610 cm^{-1} (C=C); ^{1}H NMR (DMSO-d_6) δ=3.05 (6H, s, NMe_2), 6.77 (2H, d, J=9 Hz, aromatic H), 7.05—7.58 (7H, m, aromatic H), 7.65 (1H, d, J=13 Hz, olefinic H), 8.55 (1H, d, J=13 Hz, olefinic H), 12.02 (1H, s, NH); FAB-MS m/z 378 (M^+). **6b**: blue crystals; IR (Nujol) 3150 (NH), 1695, 1635 (C=O), and 1595 cm^{-1} (C=C); ^{1}H NMR (DMSO-d_6) δ=3.06 (12H, s, NMe_2), 6.79 (2H, d, J=9 Hz, aromatic H), 6.83 (2H, d, J=9 Hz, aromatic H), 7.13 (2H, d, J=9 Hz, aromatic H), 7.32 (2H, d, J=9 Hz, aromatic H), 7.82 (1H, d, J=13 Hz, olefinic H), 8.24 (1H, d, J=13 Hz, olefinic H), 11.32 (1H, s, NH), 11.93 (1H, s, NH); FAB-MS m/z 421 (M^+).

Reaction of 4b with Malononitrile: **4b** (0.11 g, 0.37 mmol) in EtOH (20 ml) was mixed with malononitrile (0.11 ml, 5 equiv) in EtOH (20 ml). The color of the solution gradually turned from pale yellow to slightly red. The solution was successively heated to reflux for 2 h. After cooling the solution to room temperature, the resulting wine-red solution was concentration in vacuo and the red residual oil obtained was purified by column chromatography (silica gel 10 g) using chroloform-ether as eluent to give **5a** as dark red crystals (0.11 g, 85%): mp 136—137 °C; IR (Nujol) 2240 (C≡N) and 1600 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=3.06 (6H, s, NMe_2), 3.07 (6H, s, NMe_2), 6.63 (2H, d, J=9 Hz, aromatic H), 6.71 (2H, d, J=9 Hz, aromatic H), 6.94 (1H, d, J=12 Hz, olefinic H), 7.10 (2H, d, J=9 Hz, aromatic H), 7.34 (2H, d, J=9 Hz, aromatic H), 7.47 (1H, d, J=12 Hz, olefinic H); EI-MS m/z 342 (M^+). By the similar manner **3c** and **5a** were prepared from **1** or **4a**; **3c**: dark red crystals; IR (Nujol) 2210 (C≡N) and 1605 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=2.97 (6H, s, NMe_2), 6.42 (2H, d, J=9 Hz, aromatic H), 6.78—7.55 (8H, m,

aromatic and olefinic H), 7.46 (2H, d, J=9 Hz, aromatic H), 7.55—7.88 (1H, m, aromatic H); EI-MS m/z 405 (M^+). **5a**: dark red crystals; IR (Nujol) 2220 (C≡N) and 1605 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=3.06 (6H, s, NMe_2), 6.62 (2H, d, J=9 Hz, aromatic H), 7.31 (2H, d, J=9 Hz, aromatic H), 7.06—7.51 (7H, m, aromatic and olefinic H); EI-MS m/z 299 (M^+).

Reaction of 1 with 2,4-Dinitrophenylhydrazine: **1** (80 mg, 0.22 mmol) and 2,4-dinitrophenylhydrazine (44 mg, 0.22 mmol) in EtOH (5 ml) containing 1 drop of concd HCl was warmed on a steam bath for 1 h. The resulting deep-red solution was concentrated to give precipitates, which were filtered and then washed with ether to give dark-red crystals (93 mg, 79%): mp ca. 231 °C (decomp); IR (Nujol) ca. 3500 (NH), 1605 (C=C and C=N), and 1585 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ=2.99 (6H, s, NMe_2), 5.46 (1H, d, J=9.5 Hz, aromatic H), 6.63 (2H, d, J=9 Hz, aromatic H), 7.51—7.79, 8.01—8.14 (12H, m, aromatic and olefinic H), 8.49 (1H, d, J=2.5 Hz, aromatic H); EI-MS m/z 537 (M^+). **7** was prepared by the similar manner: dark red crystals; IR (Nujol) ca. 3300 (NH), 1615 (C=C and C=N), and 1590 cm^{-1} (NH); ^1H NMR δ=3.00 (6H, s, NMe_2), 6.63 (2H, d, J=9 Hz, aromatic H), 6.88 (1H, d, J=10 Hz, olefinic H), 7.14—7.49 (7H, m, aromatic H), 7.63 (1H, d, J=9 Hz, aromatic H), 7.95 (1H, d, J=10 Hz, olefinic H), 8.27 (1H, dd, J=2, 9 Hz, aromatic H), 9.07 (1H, d, J=2 Hz, aromatic H), 10.97 (1H, s, NH); EI-MS m/z 430 (M^+).

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6) The diene systems have predominantly *s*-trans, i.e., (1*E*, 3*E*)-diene configurations suggested from ^1H NMR data.

7) H^+-source is necessary in this case.

8) Cf., F. Theron, M. Verny, and R. Vessiere, "Chemistry of Carbon-Carbon Triple Bond. Part 1," ed by S. Patai, John Wiley & Sohns, New York (1978), Chap. 10.

9) The ketone **8** was easily obtained by chromatography of alcohol **1** on alumina (Merck II—III); mp 132—137 °C; IR (Nujol) 1620 (C=O) and 1590 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=2.99 (6H, s, NMe_2), 6.49 (2H, d, J=9 Hz, aromatic H), 6.67 (1H, s, olefinic H), 6.96—7.46 (8H, m, aromatic H), 7.77 (2H, d, J=9 Hz, aromatic H); EI-MS m/z 357 (M^+).