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Synthetic study of tetramethyljulolidine—a key intermediate toward the synthesis of the red dopant DCJTB for OLED applications

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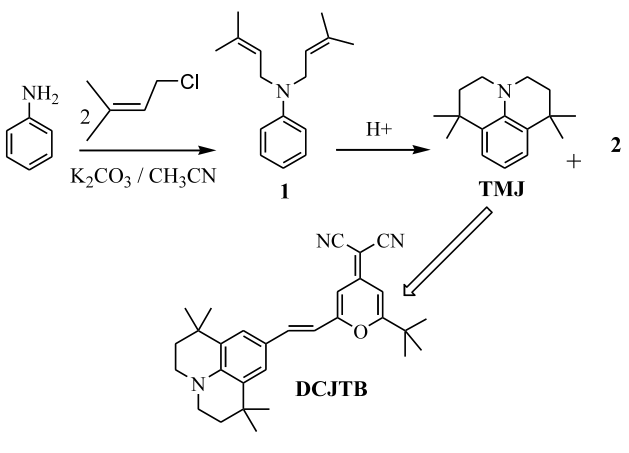
Abstract—The formation and characterization of a novel chiral sulfonic acid derivative obtained during the synthesis of 1,1,7,7-tetramethyljulolidine (TMJ), a key intermediate towards the red dopant 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) used for organic electroluminescent devices, upon bis-annulation of *N*,*N*-bis(4-methyl-2-butenyl)aniline is described. © 2002 Elsevier Science Ltd. All rights reserved.

Organic electroluminescent devices are of growing interest in various display applications due to their high luminous efficiency and capability of emitting many colors throughout the visible spectrum. Commercial interest in organic light emitting diode (OLED) technology has been the vital driving force in fueling the recent research and development activities.[1,2] 4-(Dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran, (DCJTB) is one of the best fluorescent dopants of choice for the red emitter of tris(8-hydroxyquinolinato)aluminum hosted OLEDs including Pioneer's recently demonstrated passive matrix full color prototype and Kodak/Sanyo's 2.4-in and 5.5-in low temperature poly silicon full color active matrix OLED displays. The cost of manufacturing DCJTB is prohibitively high owing to the synthetic complications of one of the key intermediates, 1,1,7,7-tetramethyljulolidine (TMJ), which can be prepared in two steps from aniline and 1-chloro-3-methyl-2-butene (Scheme 1). The low yield (~30%) obtained in the acid catalyzed bis-annulation prompted us to reinvestigate the reaction and analyze the products of the above reaction.

N,*N*-Bis(4-methyl-2-butenyl)aniline **1** was prepared by the conventional *N*-alkylation of aniline with 2 equiv. of 1-chloro-3-methyl-2-butene in the presence of K_2CO_3 at reflux. This compound was then subjected to a bis-annulation in the presence of an acid catalyst to form the key intermediate TMJ.

Different acid catalysts were employed to effect the bis-annulation. The starting material was found to remain unaffected in the presence of weak acids like *p*-toluenesulfonic acid, methanesulfonic acid and acetic acid. Strong acids such as aqueous perchloric acid, trifluoroacetic acid and trifluoromethanesulfonic acid led to the formation of TMJ in infinitesimal quantities along with an inseparable polar mixture. In the presence of concentrated sulfuric acid at 0°C, TMJ was obtained in 37% yield in addition to a major quantity



Scheme 1. Synthesis of DCJTB.

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of an insoluble material. To enhance the yield of TMJ, the temperature of the reaction was raised to about 30°C, but this led to a further decrease in the yield of TMJ (34%) accompanied by a proportionate increase in the formation of the insoluble by-product (Table 1). Moreover, in both cases, conc. sulfuric acid was used in large excess (about three v/w equivalents), which led to a voluminous precipitation during the basic work-up of the reaction, which in turn made the process of filtration more tedious. Hence, we decided to use a combination of acids to avoid these complications.

Various proportions of methanesulfonic acid and sulfuric acid were prepared (v/v equivalents—1:1, 2:1, 4:1) to catalyze the formation of TMJ. A decrease in the concentration of sulfuric acid resulted in a drastic decrease in the yield of TMJ (Table 1). However, the insoluble by-product **2** was obtained predominantly (59%) when a 1:1 mixture of methanesulfonic acid:sulfuric acid was used, which provoked our interest in characterizing and studying its formation.

The mass spectra of compound **2** showed peaks at *m*/*e* 309 (M^+) and at 229 (M^+–SO_3H+1), indicating that product **2** must bear a –SO_3H group in its skeleton. The unsymmetrical nature of the ^1H NMR spectrum suggested that the compound might have undergone an unexpected rearrangement during the acid-catalyzed bis-annulation. The ^{13}C NMR showed signals for three quaternary, four methine, five methylene and two methyl carbons. A methylene at 116.88 ppm indicated the presence of an exocyclic double bond whose protons resonated at 5.28 and 4.94 ppm as singlets. Based on a detailed analysis of both one and two C–C dimensional NMR spectra (^1H–^1H COSY, ^1H–^{13}C HETCOR), the structure was found to be consistent with structure **2** (Fig. 1).[3] It was further unequivocally confirmed by a single crystal X-ray diffraction study.[4]

A plausible mechanism for the formation of 2-(4′,4′-dimethyl-1′-phenyl-3′-piperidyl)-2-propene-1-sulfonic acid **2** is presented in Scheme 2.

The mechanism is likely to involve an acid-catalyzed intramolecular alkylation of the double bond by the first-formed carbonium ion to form the intermediate **3**. Further the exocyclic double bond of **3** undergoes sulfonation in the presence of sulfuric acid to form the sulfonic acid **2**.

To summarize, we have characterized and proposed a plausible mechanism for the formation of the by-product, a novel chiral sulfonic acid derivative **2** obtained during the synthesis of TMJ, a key intermediate towards the red dopant DCJTB for organic electroluminescent devices upon bis-annulation of *N*,*N*-bis(4-methyl-2-butenyl)aniline **1**. It was also found that **2** is a water-soluble compound and hence can be eliminated easily to furnish highly pure TMJ.

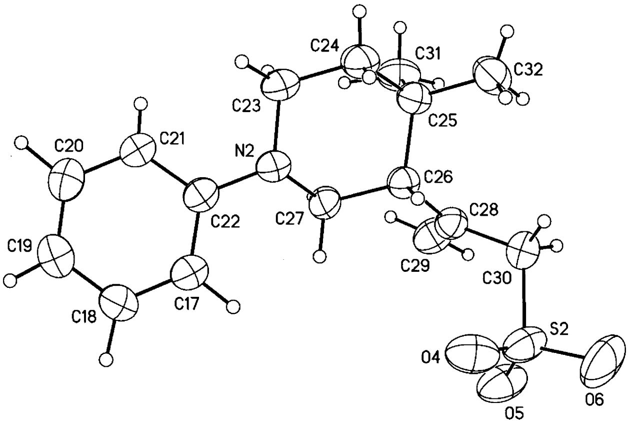
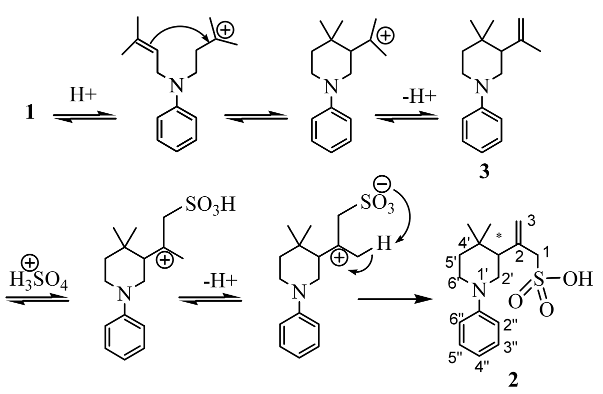


Figure 1. ORTEP diagram for compound **2**. For the sake of clarity, H atoms are not labeled.



Scheme 2.

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Table 1. Yields of TMJ and **2** obtained by catalysis using various proportions of sulfuric acid and methane sulfonic acid

Entry	Acid/solvent	Temperature (°C)	Time (h)	Yield of TMJ (%)	Yield of **2** (%)
1	Conc. H_2SO_4	0	0.5	37	20
2	Conc. H_2SO_4	0–30	3	34	22
3	H_2SO_4:CH_3SO_3H (1:1)	0	1	16	59
4	H_2SO_4:CH_3SO_3H (1:2)	0–30	3	10	22
5	H_2SO_4:CH_3SO_3H (1:4)	0–30	3	<5	–

NMR spectroscopic data and the Department of Crystallography, National Tsing-Hua University, Taiwan for single crystal X-ray diffractional analyses.

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3. Typical experimental procedure: To a mixture of methanesulfonic acid and sulfuric acid (1:1 v/v equivalents, 5 mL), *N*,*N*-bis(4-methyl-2-butenyl)aniline (**1**, 2.5 g, 11 mmol) was added at 0°C and the mixture stirred for 1 h. After complete disappearance of the starting material (monitored by TLC), the reaction mixture was poured onto ice and extracted using dichloromethane (3×300 mL). The organic layer was washed with saturated NaHCO$_3$ solution and water, dried over anh. MgSO$_4$ and the solvent was evaporated to dryness to yield TMJ (4 g, 16%). During basification of the aqueous layer of the reaction mixture using saturated NH$_4$OH solution, compound **2** crystallized as needles (2.0 g, 59%; mp 56–58°C). Spectral characteristics of **2**: ^{1}H NMR (CDCl$_3$, 500MHz) δ 0.86 (s, 3H), 0.95 (s, 3H), 1.43 (m, 1H), 1.66 (dt, $J=13.5$, 2.5 Hz, 1H), 2.55 (dd, $J=12.0$, 4.5 Hz, 1H), 2.85 (m, 2H), 3.35 (dd, $J=12.5$, 3.0 Hz, 1H), 3.45 (dd, $J=12.5$, 3.0 Hz, 1H), 3.55 (q, $J=13.25$ Hz, 2H), 4.94 (s, 1H), 5.28 (s, 1H), 6.82 (t, $J=8.0$ Hz, 1H), 6.95 (d, $J=7.8$ Hz, 2H), 7.22 (t, $J=8.0$ Hz, 2H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 19.74, 30.66 (2Me's), 32.70 (C-4′), 40.08 (CH$_2$, C-5′), 45.44 (CH$_2$, C-6′), 49.26 (CH, C-2′), 50.32 (CH$_2$, C-2′), 61.89 (CH$_2$, C-1), 116.18 (2CH's, C-2″, C-6″), 116.88 (CH$_2$, C-3), 118.96 (CH, C-4″), 129.32 (2CH's, C-3″, C-5″), 142.60 (C-2), 151.11 (C-1″).
4. Compound **2** was crystallized from acetonitrile:water. 2-(4,4-Dimethyl-1-phenyl-3-piperidyl)-2-propene-1-sulfonic acid **2** was found to be a *dl*-pair as seen from the X-ray diffractional pattern.

   Crystal data for compound **2**[F1]: C$_{32}$H$_{58}$N$_2$O$_{13}$S$_2$, M = 742.92 (*dl*-pair), monoclinic, space group $P2(1)/c$ at a temperature 294(2) K and wavelength = 0.71073 Å, $a=20.7836(18)$ Å, $\alpha=90°$, $b=9.7131(9)$ Å, $\beta=117.156(2)°$, $c=21.9556(19)$ Å, $\gamma=90°$, $U=3943.7(6)$ Å^3, $Z=4$, $D_c=1.251$ mg/m^3; absorption coefficient = 0.196 mm^{-1}, $F(000)=1600$, crystal size = 1.10×0.15×0.10 mm^3; θ range for data collection = 1.10–28.28°, index ranges $-23\leq h\leq 26$, $-12\leq k\leq 12$, $-28\leq l\leq 24$, reflections collected = 22 977, independent reflections = 8752 [$R_{\text{int}}=0.0728$], completeness to $\theta=28.28°$ is 89.6%, absorption correction = empirical, max. and min. transmission = 0.8960 and 0.4552, refinement method = full-matrix least-squares on F^2, data/restraints/parameters = 8752/0/442, goodness-of-fit on $F^2=1.124$, final R indices [$I>2\sigma(I)$] $R_1=0.0761$, $wR_2=0.2203$; R indices (all data) $R_1=0.1260$, $wR_2=0.2533$, largest difference peak and hole = 0.582 and −0.597. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 181958. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].