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Synthesis and Properties of the Tristyrylmethyl Anion

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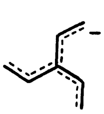
The title anion (**3**) having a C_{3v} symmetric structure was generated from newly synthesized tristyrylmethane (**4**) and was characterized by means of ^{1}H and ^{13}C NMR spectroscopy. The pK_a value of **4** was determined as 20.1 in DMSO-EtOH (9:1), indicating considerable conjugative stabilization of the anion **3**. The cyclic voltammetry of **3** in acetonitrile exhibited only irreversible one-electron oxidation peak corresponding to the formation of a chemically unstable radical species. Whereas quenching the anion **3** with H_2O or Me_3SiCl quantitatively afforded the cross-conjugated triene **6** (R=H or Me_3Si), the reaction of **3** with the tropylium ion yielded 1,1′-bicycloheptatrienyl (29%), as well as the triene **6** (R=C_7H_7) (66%), demonstrating that **3** can also acat as a one electron reductant.

Although linearly-conjugated open-chain pentadienyl anions (**1**) have been extensively studied by means of ^{1}H and ^{13}C NMR spectroscopy[1] and shown to be generally predominated by the "W" conformation, the NMR study on its cross-conjugated derivative, the 3-vinylpentadienyl anion (**2**), seems to be quite limited. For example, **2** and some of its alkylated derivatives were observed by NMR[1c,2] but no NMR data was reported for a variety of cross-conjugated carbanions with aryl substituents prepared by Kuhn *et al.*[3] Here we wish to report on the properties of the newly synthesized tristyrylmethyl anion (**3**), which can also be looked upon as a tri-vinylog of the long-known triphenylmethyl (trityl) anion.


1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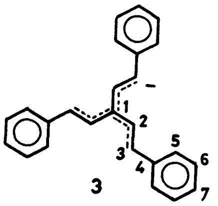
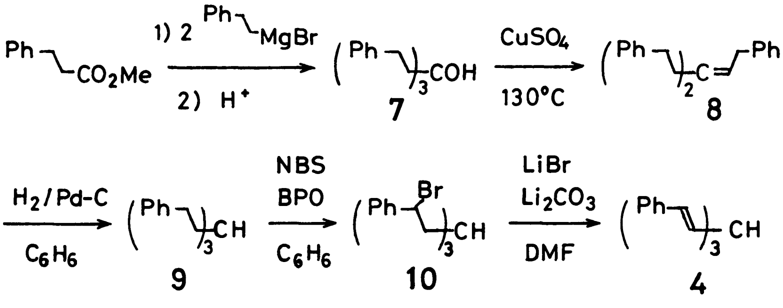


3

The parent hydrocarbon, tristyrylmethane (**4**), was synthesized in 53% overall yield from methyl 3-phenylpropanoate as shown in Scheme 1. Upon treatment with an equimolar amount of *n*-BuLi or *t*-BuOK in THF, the hydrocarbon **4** afforded a deep blue solution of the anion **3**, which was quite sensitive to air but could be stored unchanged for more than a year when sealed under vacuum.

The ^{1}H and ^{13}C NMR data for the anion **3** are shown in Table 1 together with those for the parent hydrocar-



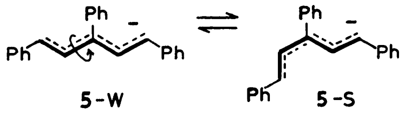
Scheme 1.

TABLE 1. ^{1}H AND ^{13}C NMR DATA FOR **3** AND **4**, AND EMPIRICAL AND CALCULATED π-ELECTRON DENSITIES (ρ) FOR **3**

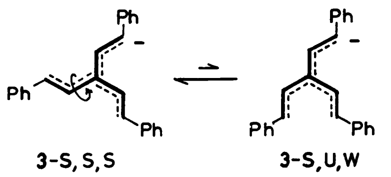
Position	δ_{H} (300 MHz)			$\delta_{^{13}\text{C}}$ (25 MHz)			ρ (**3**)	
	4$^{a)}$	**3**·K$^{+\,b)}$	**3**·Li$^{+\,b)}$	**4**$^{a)}$	**3**·K$^{+\,b)}$	**3**·Li$^{+\,b)}$	Emp$^{c)}$	Calcd$^{d)}$
1	3.96$^{e)}$	—	—	48.5	100.2	101.9	1.211	1.204
2	6.34$^{f)}$	7.10$^{h)}$	7.11$^{h)}$	130.7	131.6	132.2	1.010	1.000
3	6.52$^{g)}$	5.88$^{h)}$	5.84$^{h)}$	130.5	106.1	105.5	1.173	1.163
4	—	—	—	137.2	144.3	144.9	0.929	1.000
5	7.40	7.08	7.06	126.1	123.5	123.1	1.062	1.033
6	7.31	6.94	6.93	128.4	128.9	128.8	1.028	1.000
7	7.23	6.56	6.53	127.2	120.9	120.0	1.079	1.033

a) In $CDCl_3$. b) In THF-THF-d_8 (9:1). c) Estimated from $\delta_{^{13}\text{C}}$ of **3**·K$^+$ according to the ρ-δ relationship obtained for K$^+$ salts of open-chain carbanions: $\rho=(289.5-\delta)/156.3$ (Ref. 1e). d) Calculated by simple HMO ($\beta_{1,2}=\beta_{3,4}=0.9$). e) q ($J$=6.6 Hz). f) dd ($J$=16.2, 6.6 Hz). g) d ($J$=16.2 Hz). h) d ($J$=15.0 Hz).

bon **4**. Close similarity of the ^{1}H and ^{13}C chemical shifts for **3**·K$^+$ to those for **3**·Li$^+$ suggests that these salts exist as "loose" or "solvent-separated" ion pairs with little interaction between the cation and the anion. Remarkable upfield shifts noted for the ^{13}C NMR signals of C-1 and C-3 in **3**, as well as of C-5 and C-7 although in lesser amounts, indicate the presence of high electron densities on these carbons in agreement with the results of MO calculations (Table 1).



Scheme 2.



Scheme 3.

1,3,5-Triphenylpentadienyl anion **5** was reported to be in a rapid equilibrium between the "W" and "S" forms having comparable stability (Scheme 2) and to exhibit ^{13}C NMR line broadening at −5 °C.[1f] For the present anion **3**, the corresponding rotation of the inner bond inevitably results in the formation of the sterically unfavorable "U" shape for one of the pentadienyl moieties (Scheme 3). Thus, the ^{13}C NMR line broadening of the C-3 and C-2 signals was observed at −45 °C for **3**·Li$^+$ in THF, but at lower temperatures the C-3 signal reappeared at δ 103.7 as a sharp singlet with the relative intensity comparable to the original one, while the C-1 signal remained almost unchanged. This observation may be taken as evidence that the equilibrium shown in Scheme 3 lies far to the left favoring the symmetric structure, although at the low temperatures the C-2 signal was obscured by overlapping with the more slowly broadening phenyl signals and observation of the signals for **3**-S,U,W, if any, was precluded by the low S/N ratio resulting from decreased solubility of **3**·Li$^+$ itself.

The electronic spectrum of the anion **3** in DMSO exhibited the longest-wavelength absorption at 585 nm (log ε 4.75) with a shoulder at 540 nm (log ε 4.72). The acidity of the hydrocarbon **4**, which measures the stability of the anion **3**, was then determined on the basis of this absorption in DMSO–EtOH (9 : 1) by the spectrophotometric method of Kuhn and Rewicki[3b] using the H_- function corrected with 9-phenylfluorene (pK_a 18.5)[4,5] as a standard. The pK_a of **4** was found to be 20.1±0.2, indicating that **4** is about 10^{12} times more acidic than triphenylmethane (pK_a 32.5)[5] owing to the great conjugative stabilization of the anion **3**.

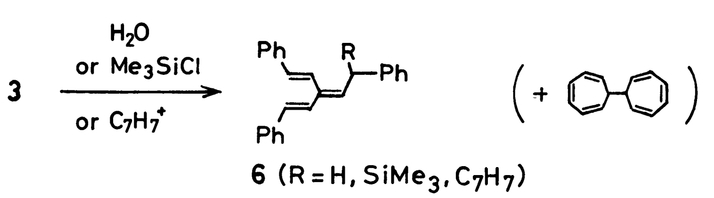
In order to compare the redox behavior of the anion **3** with that of the trityl anion, which exhibits two successive oxidation steps leading to the radical and to the cation,[6] cyclic voltammetry was conducted on the anion **3** generated with *t*-BuOK in acetonitrile. The voltammogram obtained at the scan rate of 0.1 V/s exhibited an irreversible anodic peak corresponding to the oxidation of **3** to the radical at −1.33 V *vs.* Ag/Ag$^+$, from which was estimated the $E_{1/2}$ value[7] as −1.38 V *vs.* Ag/Ag$^+$ (−1.09 V *vs.* SCE),[8] 0.11 V less negative than $E_{1/2}$ for the trityl anion (−1.20 V *vs.* SCE).[6] No peak corresponding to further oxidation of the radical was observable nor did the peak at −1.33 V become reversible upon increasing the scan rate up to 1 V/s, indicating that the radical species is chemically unstable and decomposes during measurement.

Finally, quenching reactions of the anion **3** were conducted with excessive H_2O and Me_3SiCl, and were found to give the cross-conjugated triene **6** (R=H and Me_3Si) in 100 and 79% yields, respectively (Scheme 4). In contrast, the reaction of **3**·Li$^+$ with an equimolar amount of the tropylium ion afforded 1,1′-bicycloheptatrienyl, the one-electron reduction product of the tropylium ion,[9] in 29% yield in addition to the triene **6** (R=C_7H_7) (66%). This result clearly demonstrates that the anion **3** can act not only as a nucleophile but also as a one-electron donor towards a stable carbocation.

Experimental

General. Melting points are uncorrected. The elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. The IR and visible spectra were recorded on Hitachi 215 and Hitachi 200-10 spectrometers, respectively. The ^{1}H NMR spectra were taken with a Hitachi R-24 (60 MHz) or, when specified, with a Nicolet NP-300 NB (300 MHz) spectrometer with Me_4Si as the internal standard. The ^{13}C NMR spectra were recorded on a JEOL FX-100 (25 MHz) spectrometer operated in the Fourier transform mode.

Tris(2-phenylethyl)methanol (7). A solution of methyl 3-phenylpropanoate (16.4 g; 0.100 mol) in ether (50 ml) was added dropwise over 0.5 h to a stirred solution of 2-phenylethylmagnesium bromide, prepared from 2-phenylethyl bromide (40.7 g; 0.220 mol) and Mg (5.35 g; 0.220 mol) in ether (100 ml). After refluxing for 3 h, the reaction mixture was hydrolyzed with saturated NH_4Cl and worked up in the usual way to give **7** (32.9 g; 95.5%) as white needles: mp 68.8—70.0 °C; IR (KBr) ν 3500 cm^{-1} (OH); NMR



Scheme 4.

($CDCl_3$) δ=7.20 (s, 15H), 2.67 (m, 6H), 1.86 (m, 6H), and 1.33 (s, 1H). Found: C, 86.97; H, 8.10%. Calcd for $C_{25}H_{28}O$: C, 87.16; H, 8.19%.

1,5-Diphenyl-3-(2-phenylethyl)-2-pentene (8). A stirred mixture of **7** (15.3 g; 44.3 mmol) and anhydrous $CuSO_4$ (5.39 g; 33.8 mmol) was heated at 130 °C for 0.5 h and then extracted with ether to give **8** (14.6 g; 100%) as a colorless viscous oil; IR (neat) ν 1660 cm^{-1} (C=C); NMR (CCl_4) δ=7.11 (s, 15H), 5.28 (t, 1H), 3.17 (d, 2H), and 2.9—2.2 (m, 8H).

Tris(2-phenylethyl)methane (9). A solution of **8** (15.4 g; 47.2 mmol) in benzene (50 ml) was catalytically hydrogenated over 5% Pd-C (2 g) for 2 d to give **9** (16.0 g; 100%) as a colorless viscous oil; NMR (CCl_4) δ=7.01 (s, 15H), 2.45 (m, 7H), and 1.58 (m, 6H).

Tris(2-bromo-2-phenylethyl)methane (10). A mixture of **9** (11.3 g; 34.3 mmol), *N*-bromosuccinimide (17.9 g; 101 mmol), and benzoyl peroxide (1.0 g; 4.1 mmol) in CCl_4 (60 ml) was stirred at room temperature for 1 h and at 80 °C for 1 h. The cooled mixture was filtered, evaporated, and crystallized from hexane to give **10** (11.9 g; 61.4%) as yellow crystals: NMR (CCl_4) δ=7.21 (s, 15H), 4.82 (t, 3H), and 2.15 (m, 7H).

Tristyrylmethane (4). A dried mixture of Li_2CO_3 (4.12 g; 55.8 mmol) and LiBr (4.14 g; 47.7 mmol) was added portionwise over 15 min to a stirred solution of **10** (6.00 g; 10.6 mmol) in DMF (50 ml) at 10 °C. After heating the stirred mixture at 100 °C for 1.7 h, the mixture was treated with water and worked up to give **4** (3.10 g; 90.6%) as pale brown powder. Recrystallization from hexane–benzene (1:1) afforded 2.70 g of off-white prisms: mp 110.0—111.0 °C; IR (KBr) ν 1650 cm^{-1} (C=C). Found: C, 93.00; H, 6.80%. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88%.

The Tristyrylmethyl Anion (3). *Method A (Preparation under Vacuum)*: *The NMR Spectra*; Under a stream of argon, the hydrocarbon **4** was added to an equimolar amount of *t*-BuOK or neat *n*-BuLi (obtained by evaporation of the hexane solution) in an NMR tube connected to a vacuum line. An appropriate amount of dry THF-THF-d_8 (9:1) was vacuum distilled into this mixture to give a 0.1 M solution. The tube was then sealed under vacuum and subjected to NMR measurements.

The Electronic Spectrum; A diluted solution (2.79×10^{-5} M[†]) of **4** in DMSO (5.00 ml) was placed in a 1-cm cell connected to a vacuum line. The cell was equipped with a mixing compartment containing *t*-BuOK (1 mg; 0.009 mmol). After the DMSO solution was degassed by three freeze-pump-thaw cycles, the whole assembly was sealed under vacuum, and the solution mixed with *t*-BuOK and subjected to the measurement.

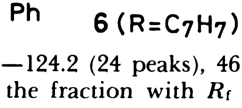
Quenching with H_2O; Water (1 ml) was vacuum distilled into a solution of $3\cdot K^+$, prepared as described above from **4** (0.0405 g; 0.126 mmol) and *t*-BuOK (0.020 g; 0.18 mmol) in THF (3 ml). The resultant pale yellow solution was worked up and purified by PTLC over SiO_2 developed with hexane-benzene (2:1) to give **6** (R=H) (0.0400 g; 100%) as a colorless viscous oil; NMR (300 MHz) ($CDCl_3$) δ=7.44—7.14 (m, 15H), 7.10 (d, *J*=16.4 Hz, 1H), 6.95 (d, *J*=15.9 Hz, 1H), 6.73 (d, *J*=16.4 Hz, 1H), 6.69 (d, *J*=15.9 Hz, 1H), 5.97 (t, *J*=7.8 Hz, 1H), and 3.69 (d, *J*=7.8 Hz, 2H).

Method B (Preparation under Nitrogen): *Quenching with Me_3SiCl*; *n*-BuLi (1.4 M in hexane) (5.0 ml; 7.0 mmol) was added to a stirred and deaerated solution of **4** (0.471 g; 1.46 mmol) in dry THF (10 ml) under dry nitrogen. To the resultant deep blue solution was immediately added Me_3SiCl (2.6 g; 24 mmol) to give a pale yellow suspension, which was evaporated, hydrolyzed, and extracted with ether. The crude product was purified by PTLC over SiO_2 developed with hexane-benzene (2:1), affording **6** (R=Me_3Si) (0.449 g; 79.0%) as a pale yellow viscous oil: NMR (300 MHz) ($CDCl_3$) δ=7.40—7.05 (m, 15H), 6.94 (d, *J*=16.2 Hz, 1H), 6.90 (d, *J*=16.2 Hz, 1H), 6.52 (d, *J*=16.2 Hz, 1H), 6.31 (d, *J*=16.2 Hz, 1H), 6.21 (d, *J*=12.0 Hz, 1H), 3.52 (d, *J*=12.0 Hz, 1H), and −0.06 (s, 9H).

The pK_a Measurements. The pK_a value was determined by the method of Kuhn and Rewicki,[3b)] using the H_- function reported by Bowden and Stewart and corrected with the known pK_a of 9-phenylfluorene (18.59).[4)] The visible spectra were measured under vacuum as described above in 5.00 ml of DMSO-EtOH (90:10 by mol, also used were mixtures of 85:15 and 80:20 by mol) using NaOEt (0.05 mmol, obtained by evaporation of 0.500 ml of a 0.1 M ethanolic solution) as a base.

Cyclic Voltammetry. The measurements were performed by the method and apparatus previously reported,[10)] on a sample solution freshly prepared by adding *t*-BuOK (0.0202 g; 0.180 mmol) to a stirred solution of **4** (0.0502 g; 0.156 mmol) and dried Bu_4NClO_4 (0.513 g; 1.50 mmol) in dry acetonitrile (15 ml) under an atmosphere of nitrogen.

Reaction of $3\cdot Li^+$ with Tropylium Tetrafluoroborate. A solution of $3\cdot Li^+$ was prepared as described above by vacuum distillation of dry THF (100 ml) into a 200 ml flask containing a stirring bar, **4** (2.90 g; 9.00 mmol), and *n*-BuLi (9.18 mmol, obtained by evaporation of 6.7 ml of 1.37 M solution in hexane). The flask was equipped with a side-arm containing tropylium tetrafluoroborate (1.60 g; 9.00 mmol). After sealing the whole equipment under vacuum, the tropylium salt was added from the side-arm into the stirred solution of $3\cdot Li^+$. The mixture was stirred for 16 h, hydrolyzed, and worked up to give the crude product, which was then separated by PTLC over SiO_2 developed with hexane–benzene (3:1). From the fraction with R_f 0.75 was obtained 1,1′-bicycloheptatrienyl (0.233 g; 28.5%) identified by spectral comparison with an authentic sample, while the fraction with R_f 0.52 afforded **6** (R=C_7H_7) (2.43 g; 65.6%) as a colorless viscous oil; ^1H NMR (300 MHz) ($CDCl_3$) δ=7.44—7.12 (m, 15), 7.06 (d, *J*=16.2 Hz, 1H, H-8), 6.87 (d, *J*=15.9 Hz, 1H, H-8′), 6.67 (d, *J*=16.2 Hz, 1H, H-7), 6.63 (d, *J*=15.9 Hz, 1H, H-7′), 6.62 (t, *J*=4.8 Hz, 2H, H-6,6′), 6.19 (dd, *J*=9.3, 4.8 Hz, 1H, H-5), 6.04 (dd, *J*=9.3, 4.8 Hz, 1H, H-5′), 5.89 (d, *J*=10.2 Hz, 1H, H-1), 5.30 (dd, *J*=9.3, 5.7 Hz, 1H, H-4), 5.07 (dd, *J*=9.3, 5.7 Hz, 1H, H-4′), 4.12 (dd, *J*=10.7, 10.2 Hz, 1H, H-2), and 2.08 (dt, *J*=10.7, 5.7 Hz, 1H, H-3); ^{13}C NMR ($CDCl_3$) δ=142.9—124.2 (24 peaks), 46.7 (d, C-2), and 44.7 (d, C-3). From the fraction with R_f 0.29 was obtained a pale yellow viscous oil (0.856 g), which is supposed to be a polymeric material having structural units derived from the tristyrylmethyl radical based on its ^1H NMR exhibiting very broad signals corresponding to phenyl and olefinic protons in a ratio of about 15:5.



6 (R=C_7H_7)

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[†] 1 M=1 mol dm^{-3}.

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