tetramethylperhydro-4,5,8a,9a-tetraazafluorene [found m/z 237.20895, $C_{13}H_{28}N_4$ requires 237.20792; ^1H NMR δ ($CDCl_3$) 0.89, (dt, J = 13.2, 11.0 Hz, $H_{ax}2$ and $H_{ax}7$), 1.00 (d, J = 6.3 Hz, 1-Me and 8-Me or 3-Me and 6-Me), 1.07 (d, J = 6.4 Hz, 3-Me and 6-Me or 1-Me and 8-Me), 1.58 (dt, J = 13.1, 3.1 Hz, $H_{eq}2$ and $H_{eq}7$), 2.60 (ddq, J = 10.6, 3.3, 6.4 Hz, H1 and H8 or H3 and H6), 2.72 (ddq, J = 11.4, 3.2, 6.4 Hz, H3 and H6 or H1 and H8), 3.27 (s, H4a and H4b), 3.78 (s, H9)], was prepared in diethyl ether by a solvent modification of the method used to prepare compounds **6**-**10**.[1] The substance was obtained in ~90% purity as a sticky white solid, mp 50-65 °C, which was not hygroscopic but could not be completely separated from impurities. Compound **16**, (1*R**,3*S**,5*R**,7*S**,8b*S**,8c*S**)-1,3,5,7-tetramethylperhydro-3a,4a,7a,8a-tetraazacyclopentano[*def*]fluorene [mp 128-130 °C; found C, 67.5, H, 10.2, N, 22.6; $C_{14}H_{26}N_4$ requires C, 67.2, H, 10.5, N, 22.4; ^1H NMR δ ($CDCl_3$) 0.96 (dt, J = 13.2, 2.7 Hz, $H_{eq}2$ and $H_{eq}6$), 1.17 (d, J = 6.9 Hz, 1-Me, 3-Me, 5-Me, and 7-Me), 1.40 (dt, J = 13.2, 11.7 Hz, $H_{ax}2$ and $H_{ax}6$), 3.25 (ddq, J = 11.7, 2.7, 7.0 Hz, H1, H3, H5, and H7), 3.61 (d, J = 2.2 Hz, H_a4 and H_a8), 3.70 (d, J = 2.2 Hz, H_b4 and H_b8), 4.76 (s, H8b and H8c)], is new and was prepared in similar fashion to **12**-**15**.[1]

Single-bond spin coupling measurements were carried out on ~0.01 M solutions in deuteriochloroform at 300 K using a Bruker AM500 instrument operating at 125.8 MHz. Couplings were determined for a spectral width of 12 500 Hz and 32 808 data points. The spectra were printed with zero fill at 24K memory, thereby giving a digital resolution of 0.4 Hz/point. Assignment of the two methine (CH) carbon signals in compounds **8**, **9**, and **13** (compounds **9**, **10**, and **19**, respectively, in ref 1) was confirmed from two dimensional CH correlation data. As expected, the signal for the bridgehead carbon in **13** was considerably sharper than that for the second methine carbon. By analogy, the sharper yet higher field methine signal from **15** was assigned to the bridgehead carbon.

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Synthesis of 4,5-Dimethyl-, 4,5,9-Trimethyl-, and 4,5,9,10-Tetramethylpyrene

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Introduction

Electrophilic reagents attack pyrene at carbons 1, 3, 6, and 8, but not at the other positions (2, 4, 5, 7, 9, and 10).[4,5] Therefore, pyrenes substituted at the latter positions must be prepared in ways other than by direct electrophilic substitution of pyrene itself.[6-8]

We previously reported the preparation of 4-alkylpyrenes such as 4-methyl-, 4-ethyl-, and 4-*n*-propylpyrene from pyrene by using the *tert*-butyl group as a positional protective group.[9,10] Here, we report the application of this method to the preparation of the titled methylpyrenes.

Results and Discussion

When 2,7-di-*tert*-butyl-4-methylpyrene (**1**), prepared from pyrene in three steps,[9] was treated with Cl_2CHOCH_3 in the presence of $TiCl_4$ as a catalyst, it gave a mixture of isomers **2a**-**c** in 87% yield. The isomer distribution of **2a**-**c** was **2a**:**2b** + **2c** = 86:14 according to GLC analysis. Isomer **2a** was isolated from this mixture in 49% yield by fractional recrystallization. In the ^1H NMR spectrum of **2a**, the methyl signal is shifted 0.28 ppm downfield to 3.17 ppm, owing to the influence of the neighboring formyl group, compared to the methyl group (2.89 ppm) of **1**, and ortho coupling (9.1 Hz) between the 9- and 10-positions is observed. Therefore, the formyl group was introduced at the 5-position. The isolation of **2b** and **2c** from this mixture was unsuccessful (Scheme I). However, the structures of the inseparable **2b** and **2c** were determined by reducing the crude mixture **2a**-**c** to a mixture of dimethylpyrenes that on further formylation and reduction gave a single trimethylpyrene **5**.

The preparation of 2,7-di-*tert*-butyl-4,5-dimethylpyrene (**3a**), 2,7-di-*tert*-butyl-4,5,9-trimethylpyrene (**5**), and 2,7-di-*tert*-butyl-4,5,9,10-tetramethylpyrene (**7**) from **2a** are shown in Scheme II.

Dimethyl derivative **3a** was obtained by reduction of **2a** with $LiAlH_4$-$AlCl_3$ in ether. Formylation of **3a** with Cl_2CHOCH_3 gave **4**, which was reduced to afford the trimethyl derivative **5** in good yield. Tetramethyl derivative **7** was obtained by formylation and reduction of **5**.

Also, the 4,5-dimethyl derivative **3a** was prepared from **2a** via the hydroxymethyl and chloromethyl derivatives **3b** and **3c** in 90 and 87% yield, respectively. Compound **3c** was easily converted to **3a** in 97% yield by reduction with $LiAlH_4$.

It was reported[11,12] that when *tert*-butylbenzene derivatives were treated with Nafion-H (DuPont) in boiling toluene, trans-*tert*-butylated benzenes and *tert*-butyltoluene were formed in excellent yields. Thus, trans-*tert*-butylation of **3a**, **5**, and **7** in the presence of Nafion-H was carried out in boiling toluene to obtain desired methylpyrenes **8a**-**c**. The results are summarized in Scheme III.

Experimental Section

Melting points are uncorrected. IR spectra were recorded as KBr pellets. ^1H NMR spectra were taken at 270 MHz in $CDCl_3$ solution. Mass spectra were recorded at 75 eV using a direct-inlet system. GLC was done on a OV-1 column (2 m). Wako C-300 silica gel was used for column chromatography.

2,7-Di-*tert*-butyl-4-methylpyrene-5-carboxaldehyde (2a). To a solution of 3.5 g (10.7 mmol) of **1** and 1.25 g (11 mmol) of

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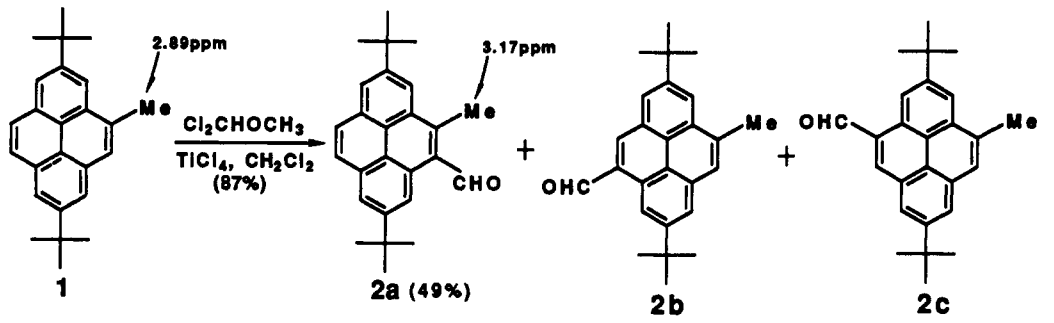
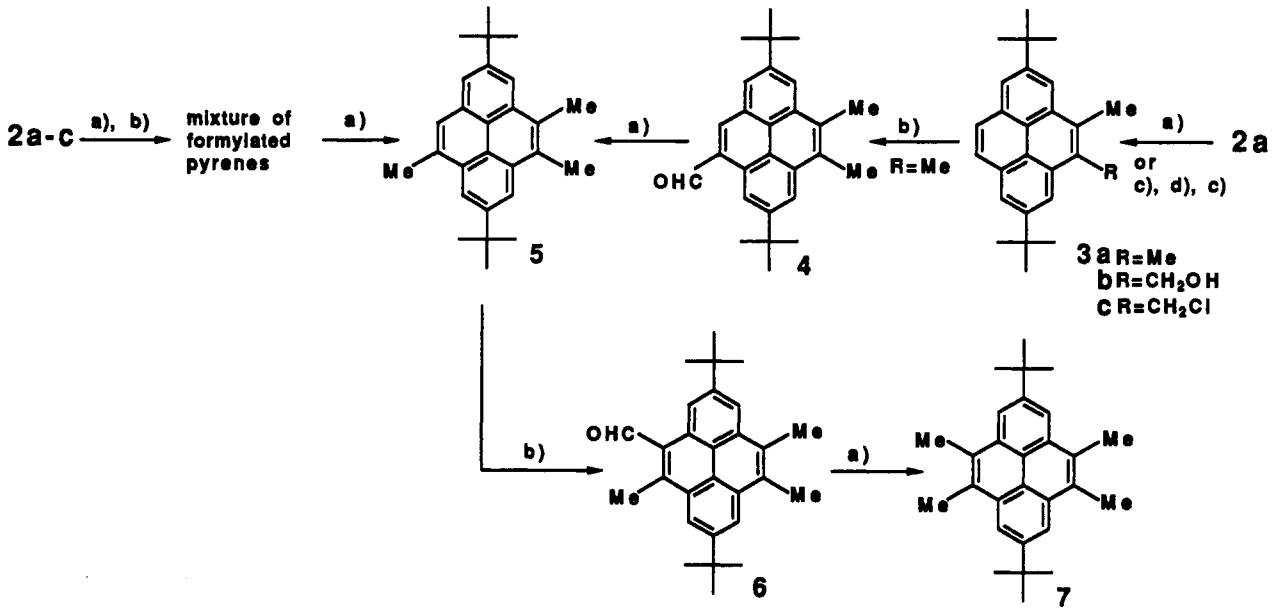
Scheme I



Scheme II[a]



[a] Key: (a) $LiAlH_4$–$AlCl_3$, Et_2O, reflux; (b) Cl_2CHOCH_3, $TiCl_4$, CH_2Cl_2, >20 °C; (c) $LiAlH_4$, Et_2O, reflux; (d) $SOCl_2$, PhH, reflux.

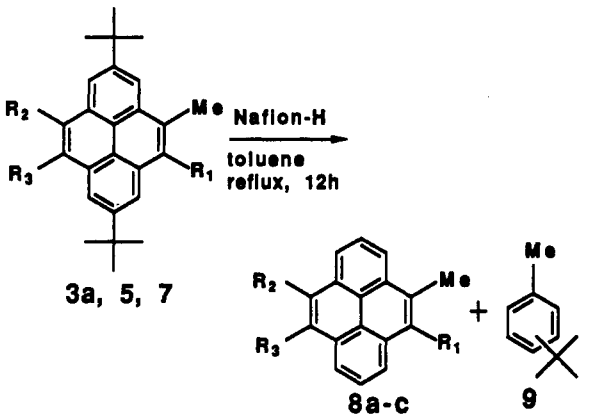
Cl_2CHOCH_3 in 150 mL of dry CH_2Cl_2 were added 5 mL (46 mmol) of $TiCl_4$ at 0 °C with stirring. The solution was warmed to room temperature, stirred for 3 h, poured into ice–water, and extracted with 200 mL of CH_2Cl_2. The organic extracts were washed with water, dried ($MgSO_4$), and evaporated in vacuo. The residue was dissolved in benzene and purified by column chromatography (hexane:benzene = 1:1) to give 3.3 g (87%) of a formylated mixture of **2a–c**. Fractional recrystallization of this mixture from hexane gave 1.88 g (49%) of pure **2a** as yellow prisms: mp 211–212 °C; IR 3050, 2950, 2850, 1660, 1595 cm^{-1}; ^1H NMR δ 1.58 (9 H, s), 1.61 (9 H, s), 3.17 (3 H, s), 8.01 (1 H, d, J = 9.1 Hz), 8.05 (1 H, d, J = 9.1 Hz), 8.22 (1 H, d, J = 1.9 Hz), 8.31 (1 H, d, J = 1.9 Hz), 8.55 (1 H, d, J = 1.9 Hz), 9.15 (1 H, d, J = 1.9 Hz), 11.27 (1 H, s); MS m/z 356 (M^+). Anal. Calcd for $C_{26}H_{28}O$: C, 87.60; H, 7.92. Found: C, 87.92; H, 7.95.

Compounds **4** and **6** were similarly prepared.

2,7-Di-*tert*-butyl-4,5-dimethylpyrene-9-carboxaldehyde (4). This compound was obtained as yellow prisms (hexane) from **3a** (1.0 g) and Cl_2CHOCH_3 (350 mg) in 83% (900 mg) yield: mp 189–192 °C; IR 2950, 2880, 1680, 1590 cm^{-1}; ^1H NMR δ 1.61 (9 H, s), 1.63 (9 H, s), 2.91 (3 H, s), 2.92 (3 H, s), 8.32 (1 H, d, J = 1.5 Hz), 8.49 (1 H, d, J = 1.5 Hz), 8.55 (1 H, d, J = 1.5 Hz), 8.58 (1 H, s), 9.72 (1 H, d, J = 1.5 Hz), 10.55 (1 H, s); MS m/z 370 (M^+). Anal. Calcd for $C_{27}H_{30}O$: C, 87.52; H, 8.16. Found: C, 87.70; H, 8.29.

2,7-Di-*tert*-butyl-4,5,9-trimethylpyrene-10-carboxaldehyde (6). This compound was obtained as yellow prisms (hexane) from **5** (700 mg) and Cl_2CHOCH_3 (250 mg) in 85% (640 mg): mp 292–295 °C; IR 2980, 2900, 1680, 1590 cm^{-1}; ^1H NMR δ 1.59 (9 H, s), 1.62 (9 H, s), 2.91 (6 H, s), 3.15 (3 H, s), 8.42 (1 H, d, J = 1.6 Hz), 8.53 (2 H, s), 9.05 (1 H, d, J = 1.6 Hz), 11.27 (1 H, s); MS m/z 384 (M^+). Anal. Calcd for $C_{28}H_{32}O$: C, 87.45; H, 8.39. Found: C, 87.73; H, 8.52.

Scheme III



entry		Substrate			Product yield (%)
		R_1	R_2	R_3	
1	3a	Me	H	H	8a (84%)[a], 9 (90%)[b]
2	5	Me	Me	H	8b (84%)[a], 9 (92%)[b]
3	7	Me	Me	Me	8c (80%)[a], 9 (95%)[b]

a) Isolated yields were shown.
b) Yields were determined by G.L.C. analysis.

2,7-Di-*tert*-butyl-4,5-dimethylpyrene (3a). To a suspension of 760 mg (20 mmol) of $LiAlH_4$ in 10 mL of absolute ether at room temperature was added a solution of 2.7 g (20 mmol) of $AlCl_3$ in 20 mL of absolute ether. To the resulting suspension was added a solution of 1.9 g (5.3 mmol) of **2a** in 60 mL of absolute ether at room temperature. The mixture was refluxed for 1 h. After

the mixture was cooled to room temperature, it was poured carefully into a large amount of ice–water and was extracted with benzene (100 mL × 2). The extract was washed with 10% aqueous HCl, water, and brine, dried ($MgSO_4$), and evaporated in vacuo. The residue was chromatographed (hexane) to give a colorless solid that was recrystallized from MeOH to afford 1.74 g (96%) of **3a** as colorless prisms: mp 232–235 °C; IR 3050, 2950, 1610, 1590 cm^{-1}; ^1H NMR δ 1.60 (18 H, s), 2.91 (6 H, s), 8.02 (2 H, s), 8.15 (2 H, d, J = 1.8 Hz), 8.38 (2 H, d, J = 1.8 Hz); MS m/z 342 (M^+). Anal. Calcd for $C_{26}H_{30}$: C, 91.17; H, 8.85. Found: C, 90.91; H, 9.07.

Compounds **5** and **7** were similarly prepared.

2,7-Di-*tert*-butyl-4,5,9-trimethylpyrene (5). This compound was obtained as colorless prisms (MeOH) from **4** (700 mg), $LiAlH_4$ (400 mg), and $AlCl_3$ (1.3 g) in 80% (538 mg) yield: mp 220–224 °C; IR 2980, 2880, 1600 cm^{-1}; ^1H NMR δ 1.58 (9 H, s), 1.61 (9 H, s), 2.90 (9 H, s), 7.87 (1 H, s), 8.08 (1 H, d, J = 1.5 Hz), 8.27 (1 H, d, J = 1.5 Hz), 8.33 (1 H, d, J = 1.5 Hz), 8.40 (1 H, d, J = 1.5 Hz); MS m/z 356 (M^+). Anal. Calcd for $C_{27}H_{32}$: C, 90.95; H, 9.05. Found: C, 91.12 H, 9.04.

This compound was also prepared from the mixture of **2a–c** according to the same procedure described previously (see Scheme II). In each step, the products were purified by column chromatography and obtained methyl or formylpyrenes were used into next step. The yields of each step were 71% (1.3 g), from the mixture of **2a–c** to dimethyl mixture, 83% (1.17 g), formylation of dimethyl mixture, and 61% (687 mg), reduction of formyldimethylpyrenes.

2,7-Di-*tert*-butyl-4,5,9,10-tetramethylpyrene (7). This compound was obtained as colorless prisms (EtOH) from **6** (860 mg), $LiAlH_4$ (400 mg), and $AlCl_3$ (1.4 g) in 90% (743 mg) yield: mp 251–257 °C; IR 3020, 2980, 2880, 1600 cm^{-1}; ^1H NMR δ 1.61 (18 H, s), 2.91 (12 H, s), 8.36 (4 H, s); MS m/z 370 (M^+). Anal. Calcd for $C_{28}H_{34}$: C, 90.75; H, 9.25. Found: C, 90.78; H, 9.22.

2,7-Di-*tert*-butyl-4-methyl-5-(hydroxymethyl)pyrene (3b). To a suspension of 500 mg (13.2 mmol) of $LiAlH_4$ in 20 mL of absolute ether was added 790 mg (2.2 mmol) of **2a** in 30 mL of absolute ether at room temperature during 30 min. After the addition was completed, the mixture was heated under reflux for 3 h and was cooled to room temperature. Then, the mixture was poured into a large amount of ice–water and was extracted with benzene. The extract was washed with 10% aqueous HCl and brine, dried ($MgSO_4$), and evaporated in vacuo. The residue was recrystallized from hexane to afford 718 mg (90%) of **3b** as colorless prisms; mp 206–208 °C; IR 3340, 3030, 2950, 1600 cm^{-1}; ^1H NMR δ 1.60 (18 H, s), 3.02 (3 H, s), 5.48 (2 H, s), 8.02 (2 H, s), 8.17 (1 H, d, J = 1.4 Hz), 8.22 (1 H, d, J = 2.2 Hz), 8.44 (1 H, d, J = 2.2 Hz), 8.57 (1 H, d, J = 1.4 Hz); MS m/z 358 (M^+). Anal. Calcd for $C_{28}H_{30}O$: C, 87.10; H, 8.44. Found: C, 87.04; H, 8.67.

2,7-Di-*tert*-butyl-4-methyl-5-(chloromethyl)pyrene (3c). To a solution of 2.88 g (8.0 mmol) of **3b** in 80 mL of benzene were added 5.0 mL of $SOCl_2$ and then 0.5 mL of pyridine. After the mixture was stirred for 1 h at room temperature and refluxed for 1 h, it was poured into ice–water and extracted with benzene. The extract was washed with 10% aqueous $NaHCO_3$ (100 mL × 3) and water, dried ($MgSO_4$), and evaporated in vacuo. The residue was recrystallized from hexane to afford 2.68 g (87 %) of **3c**: brown prisms; mp 165–166 °C; IR 3030, 2960, 2950, 1600 cm^{-1}; ^1H NMR δ 1.59 (9 H, s), 1.61 (9 H, s), 2.99 (3 H, s), 5.39 (2 H, s), 8.01 (2 H, s), 8.17 (1 H, d, J = 1.8 Hz), 8.21 (1 H, d, J = 1.8 Hz), 8.43 (1 H, d, J = 1.4 Hz), 8.46 (1 H, d, J = 1.4 Hz); MS m/z 376 (M^+), 378 (M + 2). Anal. Calcd for $C_{26}H_{29}Cl$: C, 82.84; H, 7.75. Found: C, 82.54; H, 7.99.

2,7-Di-*tert*-butyl-4,5-dimethylpyrene (3a) from 3c. To a suspension of 1.0 g (26 mmol) of $LiAlH_4$ in 30 mL of absolute ether was added dropwise 2.68 g (7.8 mmol) of **3c** at room temperature with stirring. After the addition was completed, the mixture was refluxed for 3 h and cooled. It was poured into a large amount of ice–water and was extracted with benzene. The extract was washed with water and brine and then evaporated. The residue in 10 mL of benzene was purified by column chromatography (hexane) to give 2.38 g (97%) of **3a**.

General Procedure for the Trans-*tert*-butylation of 2,7-Di-*tert*-butylmethyl-Substituted Pyrenes. A mixture of 2,7-di-*tert*-butylmethyl-substituted pyrenes (200 mg) and Nafion-H (200 mg) in toluene (5 mL) was refluxed for 12 h. The Nafion-H was then filtered from the cooled mixture, and the filtrate was concentrated in vacuo. The residue was chromatographed (hexane) to afford a colorless solid that was recrystallized from EtOH in all cases.

4,5-Dimethylpyrene (8a): (84%, 113 mg); colorless prisms; mp 206–208 °C (lit.[13] 210.5–211.5 °C).

4,5,9-Trimethylpyrene (8b): (84%, 115 mg); colorless prisms; mp 165–167 °C (lit.[14] 173 °C).

4,5,9,10-Tetramethylpyrene (8c): (80%, 112 mg); colorless prisms; mp 250–254 °C; IR 2950, 2900, 1590, 1450, 1360, 1340, 1250, 1080, 880, 790, 700 cm^{-1}; ^1H NMR δ 2.90 (12 H, s), 7.90 (2 H, t, J = 7.7 Hz), 8.06 (4 H, d, J = 7.7 Hz); MS m/z 258 (M^+). Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.82; H, 6.67.

Nucleophilic Substitution of Chlorine in Triphenylmethyl Radicals. "Reverse Effect" and a Related Single-Electron Transfer

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The "inert carbon free radicals" (IFRs) are trivalent carbon species that not only are completely disassociated, but their half-life times in solution, in contact with air, are on the order of 100 years.[1] They are also provided with an astonishingly high thermal stability (up and beyond 300 °C in air) and chemical inertness vs hydrogen donors, NO, NO_2, Cl_2, Br_2, concd. H_2SO_4, etc. Perchlorotriphenylmethyl radical (PTM•) is the paradigm of the IFRs (Scheme I).[2]

Red 4-(dimethylcarbamoyl)tetradecachlorotriphenylmethyl radical (Me_2NCO-PTM•) was synthesized by the reaction of acid chloride (ClCO-PTM•) in THF with dimethylamine, in the study of SETs between chlorinated triphenylmethyl radicals and triphenylmethyl anions (Scheme III).[3] A small proportion of a *green* radical was obtained suggesting that a simultaneous nucleophilic substitution of chlorine by the dimethylamino group had also taken place. In fact, the vast majority of highly chlorinated perchlorotriphenylmethyl radicals, except green 4-aminotetradecachlorotriphenylmethyl radical (NH_2-PTM•),[4] are red. Accordingly, it is well-known that, on account of the cumulative inductive effect of their numerous chlorines, perchlorinated aromatic substrates are susceptible to substitution by nucleophiles (S_NAr).[5-7,8b] In this connection it is mentioned that nucleophilic substitutions are believed to proceed via either polar or SET ($S_{RN}1$) pathways.[9]

Consequently, the reaction of radical PTM• with a saturated solution of dimethylamine in THF, at room temperature, has been investigated. The product consists in an inseparable mixture of PTM• and αH-tetradeca-

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